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NOAEC	No-Observed Adverse Effect Concentration
NOAEL	No-Observed Adverse Effect Level
OC	Organic Carbon
ODNR	Ohio Department of Natural Resources
Ohio EPA	Ohio Environmental Protection Agency
ONWQC	Ohio Numeric Surface Water Quality Criteria
OME	Ontario Ministry of the Environment
OMZA	Outside the Mixing Zone Average
OMZM	Outside the Mixing Zone Maximum
OU	Operable Unit
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCOI	Potential Chemical of Interest
PEL	Probable Effect Level
PRP	Potentially Responsible Party
PUF	Plant Uptake Factor
QA/QC	Quality Assurance/Quality Control
QHEI	Qualitative Habitat Evaluation Index
QSAR	Quantitative Structure–Activity Relationship
RBC	Risk-Based Concentration
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
RM	River Mile
ROI	Receptor of Interest
SAV	Secondary Acute Value
SCV	Secondary Chronic Value
SD	Standard Deviation
SEM	Simultaneously Extractable Metals
SLERA	Screening-Level Ecological Risk Assessment
SOW	Statement of Work
sp.	Species (singular)
spp.	Species (plural)
SQB	Sediment Quality Benchmark
STORET	Storage and Retrieval System for water quality data, U.S. EPA
SVOC	Semi-Volatile Organic Compound
SW	Surface Water
TDS	Total Dissolved Solids
TEL	Threshold Effect Level
TI	Toxic Index
TIC	Tentatively Identified Compound
TOC	Total Organic Carbon
TRV	Toxicity Reference Value
TSD	Technical Support Document
UCL	Upper Confidence Limit
UF	Uncertainty Factor
µg/L	Micrograms per Liter
µg/kg-day	Micrograms per Kilogram per Day
U.S. EPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service

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USGS	United States Geological Survey
VOC	Volatile Organic Compound
WPCP	Water Pollution Control Plant
ww	Wet Weight
WWH	Warmwater Habitat

EXECUTIVE SUMMARY

This Lake Erie and Grand River Baseline Ecological Risk Assessment (ERA) was conducted to evaluate ecological exposure pathways and risks associated with Lake Erie, the Grand River, and the potential for the Site to impact these water bodies. This risk assessment addresses current and reasonably anticipated future conditions, assuming no remediation is conducted. Additional property-specific risk assessments will be prepared and submitted separately to address potential soil exposures at defined Operable Units (OUs) to support feasibility studies for these OUs. When combined with the OU risk assessments, the Lake Erie and Grand River Baseline ERA will address all potential exposures and associated risks for the Site.

The reach of the Grand River flowing through the Painesville Site has generally attained applicable aquatic life use designations upstream of RM 4.2, while below this point the river has a history of partial attainment and non-attainment in various sampling locations. Of particular concern is sampling location GR-6 at RM 3.5, which was in non-attainment of its aquatic life use in 2000, 2001 and 2002; RM 3.9 was also in non-attainment in 2000, and only in partial attainment in 2001. This nonattainment can be attributed to a number of possible stressors such as water quality (exceedences of the TDS and hexavalent chromium standards), lacustuary effects, and habitat quality and changes.

Total Dissolved Solids (TDS) have decreased in mean concentration and in variability from the 1960's, when concentrations of TDS in the Grand River routinely exceeded 1,500 mg/l both within the study area and in segments downstream, to the present. Infrequent exceedances of surface water quality standards have been observed in later years. For example, there have been only two exceedances of the TDS water quality standard out of over 360 samples taken during the Phase I and Phase II sampling events (1997 – 2001). These two exceedances were located at RM 4.7, a location adjacent to the final drainage area of former Settling Basin #4. This overall decreasing trend in TDS is expected to continue, but potential sources of TDS (e.g., Solvay) will continue to exist. Infrequent, localized exceedances of TDS could be having an impact on aquatic life in the Grand River, and may partially explain the non-attainment and partial-attainment of aquatic life use seen in portions of the river.

Potential releases of COIs from groundwater discharges to the Grand River and Lake Erie were evaluated using BIOSCREEN, a U.S. EPA groundwater fate and transport model. The predicted surface water concentrations at the point of discharge were compared to surface water quality standards for the protection of aquatic life and wildlife. All chemicals detected in groundwater at concentrations above their respective Outside Mixing Zone Average (OMZA) water quality standards were evaluated for their potential to migrate and discharge into Lake Erie and/or the Grand River, with assistance from OEPA. The BIOSCREEN model was used to predict concentrations of chemicals of interest in groundwater at the point of discharge to surface water, assuming the maximum detected concentrations in each well migrate to the Lake and/or River by the shortest groundwater flow path. Model predicted concentrations at the points of discharge were compared to OMZA surface water quality standards for the protection of aquatic life and wildlife. Model predicted concentrations at the points of discharge to the Grand River exceed the OMZA surface water quality standards for nine chemicals (antimony, arsenic, barium, chromium VI, copper, cyanide, selenium, mercury and vanadium). Model predicted concentrations at the point of discharge to Lake Erie exceed the OMZA surface water quality standards for eight chemicals (antimony, carbon tetrachloride, chloroform, cobalt, cyanide, methylene chloride, selenium and silver).

Measured Cr (VI) concentrations in the Grand River exceed the chronic surface water quality criterion frequently, although the majority (83%) of these exceedances are two times the chronic surface water quality standard or less. Cr (VI) appears to be entering the Grand River adjacent to Study Area 6. The majority (70%) of the observed exceedences of the chronic water quality standard for hexavalent chromium occurred adjacent to or immediately downstream of Study Area 6; average hexavalent chromium concentrations were low upstream of the Site, increased sharply beginning at approximately RM 4.2 (in proximity to Study Area 6), peaked at RM 3.9 and dropped downstream of RM 3.1 (below Study Area 4, at the Site boundary). In addition, analysis of self-monitoring data submitted by the City of Painesville WPCF has found that exceedences of the OMZA for Cr (VI) have been detected in 25% of the grab samples collected downstream of the WPCF outfall, and that the OMZM for Cr (VI) has been exceeded in 11% of the samples collected between 1995 and 2002. There have been few instances of detectable concentrations of Cr (VI) in the Painesville WPCF effluent, indicating that the source of the Cr (VI) in the downstream ambient samples came from upstream of the treatment plant discharge location. Exceedences of hexavalent chromium standards are thus evident across a large portion of the Grand River Study Area and impacts are also evident downstream of the Study Area. Study Area 6 is a regulated landfill that contains chromium ore processing residue. Frequent exceedances of water quality standards protective of aquatic life for Cr (VI) in the Grand River, particularly in the immediate vicinity of Study Area 6, pose a potential risk to aquatic life.

Risks to benthic invertebrates from sediment in the Grand River are indeterminate for most PAHs, but naphthalene was detected at a concentration above the consensus-based sediment quality guidelines (SQGs) Probable Effects Concentrations (PEC) at three locations. These exceedances fit into a category specified by MacDonald et al. (2000) and Ingersoll et al. (2000) as having probable toxicity to benthic invertebrates. The locations where PAHs were detected in Grand River sediments are adjacent to Study Areas 4, 5 and 6. These Study Areas are not currently or historically the location of activities generating PAHs, and thus are not considered potential sources of these compounds.

Based on a comparison to consensus-based sediment quality guidelines (SQGs), detected concentrations of individual PAHs and total PAHs in Lake Erie sediment fit into a category specified as having probable toxicity to benthic invertebrates. However, the BIOSCREEN groundwater model did not show groundwater as a source of PAHs discharging to Lake Erie above surface water quality standards. A potential route for PAHs to enter Lake Erie sediments, although a route not examined in this Risk Assessment, is surface runoff from the Site to Lake Erie. However, there are many other potential sources of both runoff and PAHs in Lake Erie sediment that are not associated with the Site.

Based upon the results of this Lake Erie and Grand River Baseline ERA, it is concluded that the following chemicals detected in groundwater at the Site should be evaluated in the Feasibility Study (FS) because their model predicted concentrations exceed OMZA surface water quality standards for the protection of aquatic species and/or wildlife at the point of discharge to either Lake Erie or the Grand River:

- **Grand River**
  - Antimony
  - Arsenic
  - Barium
  - Hexavalent chromium
  - Copper
  - Cyanide
  - Selenium
  - Mercury
  - Vanadium

- **Lake Erie**
    - Antimony
    - Carbon tetrachloride
    - Chloroform
    - Cobalt
    - Cyanide
    - Methylene chloride
    - Selenium
    - Silver

1.0 INTRODUCTION

This report presents the partial Lake Erie and Grand River Baseline Ecological Risk Assessment for Site-Wide Issues (Lake Erie and Grand River Baseline ERA) at the Diamond Shamrock Painesville Work Site (Site) (Figure 1-1), namely the ecological exposure pathways and risk associated with potential impacts of sediments and groundwater at the Site to Lake Erie and the Grand River. Property-specific risk assessments will be submitted separately to address potential soil exposures at defined Operable Units (OUs) to support feasibility studies based on planned property development and use at each OU. In keeping with the National Contingency Plan (NCP) and the approved Work Plan for the Site, these property-specific risk assessments will be submitted for review by Ohio EPA prior to conducting feasibility studies. When taken together, this risk assessment for Lake Erie and Grand River site-wide issues combined with the Operable Unit risk assessments will address all potential exposures and risk for the entire Site.

This Lake Erie and Grand River Baseline ERA was prepared on behalf of the Painesville Potentially Responsible Party (PRP) Group to evaluate the nature and extent of ecological risks associated with chemicals in surface water and sediment (Figure 2-1). The Lake Erie and Grand River Baseline ERA incorporates data collected during both the Phase I and Phase II Remedial Investigations (RI) of the Painesville Site.

The Lake Erie and Grand River Baseline ERA was prepared in a manner consistent with the *Work Plan for the Human Health and Ecological Risk Assessment for the Painesville Works Site* as well as other applicable Ohio Environmental Protection Agency (Ohio EPA) and United States Environmental Protection Agency (U.S. EPA) guidance and criteria for ecological risk assessment (e.g., U.S. EPA 1989a,b; U.S. EPA 1992; U.S. EPA 1994a,b,c; U.S. EPA 1995a; U.S. EPA 1996a; U.S. EPA 1997a; Ohio EPA 1996). The Lake Erie and Grand River Baseline ERA is consistent with the Screening Level Ecological Risk Assessment (SLERA; ChemRisk 1999), included as Appendix K-II of the *Phase I Remedial Investigation Report, Volume I,* which was submitted in March of 1999 (Phase I RI; SECOR, 1999). Comments to the SLERA made by the Ohio EPA (Ohio EPA: October 7, 1998, January 29, 1999 and August 29, 2001) have been addressed through written and verbal communications with Ohio EPA, and all revisions requested by Ohio EPA have been incorporated into the methods used for this Lake Erie and

Grand River Baseline ERA. Please note that the SLERA was not approved as a final document by the Ohio EPA.

1.1 Purpose and Objectives

The purpose of the Lake Erie and Grand River Baseline ERA is to evaluate ecological risks posed by site-related chemicals, based on current site conditions for current land uses, *i.e.*, assuming no additional remedial actions are taken at the Painesville Site. The specific objectives of this Lake Erie and Grand River Baseline ERA are to:

- Identify and evaluate baseline risks (defined as risks that might exist if no remedial actions were implemented at the site);
- Identify what areas of the Painesville Site may require corrective actions; and
- Provide a basis for evaluating various redevelopment alternatives.

The Lake Erie and Grand River Baseline ERA provides an evaluation of the nature and extent of possible ecological effects based on knowledge, through 2001, of environmental conditions and of organisms that are known to be or may be present at the Site or in Lake Erie adjacent to the Site, and provides scientifically defensible support for managing the ecological resources at the Site.

1.2 Conceptual Approach to Ecological Risk Assessment

This Lake Erie and Grand River Baseline ERA is prepared in accordance with the Ohio EPA's *Generic Statement of Work (SOW) for Remedial Investigation/Feasibility Study (RI/FS)*, State Version, May 26, 1992 (Ohio EPA, 1992) and with other general methods for ecological risk assessment (U.S. EPA, 1989a; 1992; 1996a; 1997a). These conceptual approaches to ecological risk assessment involve: (1) defining the system to be studied, (2) identifying the study's goals and objectives, (3) providing the details of the analysis, and (4) describing conclusions of the analysis. In current practice, the conceptual framework for ecological risk assessment (Figure 1-2) includes three major components: problem formulation, analysis, and risk characterization. This Lake Erie and Grand River Baseline ERA is organized according to these three components.

Problem Formulation is a process to define the specific issues addressed in an ecological risk assessment. For this Lake Erie and Grand River Baseline ERA, problem formulation (Section 2.0) includes:

- Characterizing the ecological resources at the Site – Identifying water quality criteria exceedances in the Grand River and Lake Erie and evaluating aquatic life use attainment for the Grand River.
- Identifying receptors of interest (ROIs)—a limited number of specific types of ecological resources—and the exposure pathways through which receptors contact chemical stressors;
- Identifying preliminary chemicals of interest (COIs)—chemicals that might pose a risk of adverse ecological effects—in surface water, sediment, and in the food-web;
- Selecting relevant assessment endpoints—goals for environmental management and the basis for decision-making—based on the COIs, complete exposure pathways, and ROIs; and
- Formulating conceptual site models to establish the exposure pathways that are evaluated in the Lake Erie and Grand River Baseline ERA and to define the relationships among the assessment endpoints.

Analysis includes exposure characterization and effects characterization. For this Lake Erie and Grand River Baseline ERA, analysis includes:

- Exposure characterization (Section 3.0)—quantifying the concentrations (or doses) of COIs that ROIs might contact via each identified exposure pathway—based on either measured concentrations of COIs or mathematical models of the bioaccumulation of COIs through the food-web; and
- Effects characterization (Section 4.0)—quantifying the concentrations (or doses) of COIs that might be associated with adverse effects—for COIs that are components of complete exposure pathways.

Risk Characterization is the integration of the exposure and effects information to identify the nature and extent of ecological risks, if any. For this Lake Erie and Grand River Baseline ERA, risk characterization (Section 5.0) includes:

- Risk estimation—a mathematical expression of the relationship between exposure and effect—for each combination of COI, exposure pathway, and ROI;

- Uncertainty analysis—identifying variability and uncertainty in the exposure and effects characterizations—to characterize factors influential to the risk estimates; and

- Risk interpretation—a weight-of-evidence interpretation of the Lake Erie and Grand River Baseline ERA results—including consideration of risk estimation, spatial considerations, uncertainty analysis, and site-specific information. Risk interpretation concludes with the identification of receptors, study areas, and chemicals of interest (COIs) that may require corrective actions.

2.0 PROBLEM FORMULATION

Problem formulation is a systematic planning process that identifies the major factors to be considered in an ecological risk assessment (U.S. EPA, 1996a). Problem formulation includes site characterization, selection of receptors of interest, identification of preliminary chemicals of interest, identification of assessment and measurement endpoints, and development of a conceptual site model.

2.1 Site Characterization

The Painesville Site is located in Lake County, Ohio and is situated on approximately 452 ha (1130 acres) of land. The site is bordered by Lake Erie to the north, Elm Street to the south, East Street to the west, and industrial property and the Grand River to the east (Figure 2-1). Seven terrestrial study areas and two aquatic study areas are identified within the site for this Lake Erie and Grand River Baseline ERA (SECOR, 1997). This section describes terrestrial land cover types, aquatic and terrestrial study area characteristics, and aquatic and terrestrial ecological resources of the Site.

2.1.1 Terrestrial Land Cover

The Lake Erie and Grand River Baseline ERA does not consider possible risks to ecological receptors originating from soils on the Site. However, a consideration of terrestrial land cover is useful for considering possible effects on the Grand River and Lake Erie from surface runoff.

Terrestrial land cover and vegetation associations at the Site are summarized based on a review of existing information, agency consultation, and the results of a limited and qualitative field reconnaissance (SECOR, 1997). Land cover types observed in the seven terrestrial study areas at the Painesville Site were mapped onto an existing base map (Figure 2-2). Although mapped land cover habitat types were not quantitatively surveyed, the field reconnaissance data are sufficient for the purposes of this Lake Erie and Grand River Baseline ERA because they allow a general characterization of the extent of each type in each study area (Table 2-1). Land cover classifications are generally based on vegetation types rather than land use or zoning. The land cover types used to characterize the terrestrial areas of the Site include:

Old field: Old field land cover generally represents the earliest stage of a successional continuum. Vegetation is largely composed of weedy, invasive grasses and forbs; representative species include various grasses (*e.g.*, *Poa* spp., *Setaria* spp.), goldenrods study area adjacent to the Painesville Site is defined as including river miles (RM) 5.4 to 2.8. The Ohio EPA designates the Grand River as Exceptional Warmwater Habitat upstream of RM 5.5 and Warmwater Habitat downstream of RM 5.5 (Ohio EPA, 1995). Downstream of RM 4.7, the river is classified as a Lake Erie estuary and harbor area, based on interim Ohio EPA guidance (Ohio EPA, 1995).

The Lake Erie shoreline forms the northern boundary of Study Areas 1, 2 and 3. A 300 m shoreline protection system protects the One-Acre Landfill in Study Area 3 (SECOR, 1997). Lake Erie is designated by the Ohio EPA as Exceptional Warmwater Habitat, a state resource water, a public water supply, an agricultural water supply, an industrial water supply, and as bathing waters (Ohio EPA, 1997).

Study Area 1 was the primary location for the historical manufacture of soda ash from limestone using the Solvay process. Other chemical manufacturing processes conducted in this area include the manufacture of chlorine and caustic soda (using diaphragm cells), hydrochloric acid, carbon tetrachloride, Chlorowax (chlorinated paraffin wax), purified calcium products (mainly limestone fines, chalk, *etc.*), sodium bicarbonate, sodium sulfate, aluminum hydroxide, liquid hydrogen, and cement. Other products manufactured include polyvinyl chloride, vinyl chloride monomer, ammonium hydroxide, aluminum smelting, and various commercial and light industrial operations. In addition, steam and electricity were generated on site using coal fired-boilers. Recently, Dartron Corporation operated a metal recycling operation on 12.4 acres of Study Area 1. This parcel was formerly used by Martin Marietta and Uniroyal Chemical Company, Inc. to manufacture vinyl chloride monomer and polyvinyl chloride. Aluminum Smelting and Refining Company, Inc. (ASR) owns a metal smelting operation on 24 acres of Study Area 1. This parcel is now operated by Philip Metals (the current leaseholder) and was the former Diamond Shamrock Portland Cement Plant. Adjacent to the ASR site is land owned and operated by PVS Chemicals. This site was used to store waste acid from steel manufacturers. Norfolk and Western Railway Company has operated a roundhouse maintenance yard and rail spurs in Study Area 1 since 1936.

In 1986, buildings that housed soda ash, carbon tetrachloride, and electricity production were demolished, and a clay cap was placed over Study Area 1, consisting of a 6 in to >2 ft thick layer of natural clay material excavated from nearby fly-ash disposal pits. The clay layer was topped with soil, and the area was re-vegetated. Current activities at Study Area 1 involve light industrial and commercial operations. Of the 166 acres in Study Area 1, 46% is industrial, 33% is maintained (the clay-capped area), 20% is old field, and the remaining 1% is mixed old field and shrub-scrub.

Study Area 2 is currently owned by Ace Lakefront Properties. Coal coking operations were conducted at this location from 1924 to 1976 by Diamond Shamrock Chemicals Company and from 1976 to 1982 by Erie Coke and Chemical Company (now known as Scepter Management Corporation). Ace Lakefront Properties has partially demolished the abandoned coal coking plant. Study Area 2 is approximately 41 acres in size and contains approximately 76% old field and 24% industrial land cover.

Study Area 3 is owned, and to be maintained for perpetuity, by Tierra Solutions Incorporated. The study area includes a hazardous waste landfill (the One-Acre Landfill) and surrounding property. The One-Acre Landfill accepted laboratory materials from Diamond Shamrock research operations, and was closed in 1989. The landfill's multimedia cap includes a high-density polyethylene liner, a 36-inch clay layer, an 18-inch topsoil layer, and vegetation (SECOR, 1997). The landfill is surrounded by a 36-inch slurry-wall. Since the durable cap and slurry wall prevent ecological exposures to chemicals in the landfill, the One-Acre Landfill portion of Study Area 3 is not evaluated in the Lake Erie and Grand River Baseline ERA. Study Area 3 is approximately 27.76 acres in size and consists primarily of old field land cover (93%), with the remainder consisting of the maintained landfill cap (7%).

Study Area 4 was formerly used as a settling basin for the treatment of Solvay process residues (essentially limestone fines and chlorides suspended in water) from soda-ash manufacturing operations at Study Area 1 (SECOR, 1997). The basin also received waste pickle liquor (hydrochloric acid used to clean steel surfaces) and fly ash and bottom ash from coal-fired power generation facilities (operated by Cleveland Electric Illuminating Company and Diamond Shamrock). Environmental Brine Services, Inc. formerly operated a brine disposal injection well and storage tanks on 15 acres of land along the northwest portion of Study Area 4. The southern portion of Study Area 4 contains a 6.1 ha (15 acre) former municipal landfill for the Village of Fairport Harbor, which operated from the 1950s to the late 1980s. A 1.1 ha (2.7 acre) area in the southwest corner of Study Area 4 was formerly owned by Diamond Alkali and now consists of baseball fields owned by the Fairport Board of Education. Several commercial and light-industry businesses are located along the eastern and northern edges of the study area. The remainder of the land in Study Area 4 is either vegetated or has "unauthorized" dirt bike trails (SECOR, 1997). Land cover in Study Area 4 (178 acres) consists of approximately 27% old field, 27% mixed old field and shrub-scrub, 12% shrub-scrub, 8% mixed shrub-scrub and forested land covers, 2% forest, 3% bare ground (dirt bike trails) with trees, 9% maintained (former landfill), 4% recreational, and 8% industrial areas.

The southeastern border of Study Area 4 is formed by the Grand River. The Solvay process waste along this edge of Study Area 4 is not contained by a constructed berm in contrast to Study Area 7, and forms a steep ridge or bluff at the edge of the river for the length of the border. Although the river has not apparently directly eroded this ridge, the exposed face of the Solvay process waste is subject to erosion during rain events. The Solvay process waste in Study Area 4 is dry, and apparently finished draining many years ago.

Study Area 5, the former "Hydroretention Basin," consists of land formerly used as a secondary settling basin for Solvay process residues from soda-ash manufacturing operations at Study Area 1. The basin also received 70 to 90 million gallons of non-contact cooling water per day from the Solvay process facilities and the power plant (SECOR, 1997), relatively low volumes of wastes from other processes, and debris from the demolition of buildings in Study Area 1. A minimum of two feet of clay was placed over the entirety of the former settling basin contained in Study Area 5 during the 1980s. Upon placement of the clay cover, a vegetative cover was established over the entire surface area of Study Area 5 to control erosion. Study Area 5 is approximately 29 acres in size, of which 79% is old field and 21% is shrub-scrub.

The Grand River forms the southern border of Study Area 5.

Study Area 6, the former "Settling Basin #2," accepted Solvay process residues generated from soda-ash manufacturing operations at Study Area 1. The study area also contains chromite ore processing residue (COPR) from chromium product operations that occupied the eastern portion of the study area (SECOR, 1997). On July 14, 1983, the U.S. EPA enacted an Administrative Order of Consent (United States District Court of the Northern District of Ohio, Civil Action No. C80-1857) for Study Area 6. Closure activities occurred between 1974 and 1983. Closure involved covering 90 acres of land with a minimum of 36 inches of fly ash, 36 inches of clay, topsoil, and vegetation. The entire study area is approximately 149 acres.

As part of the Administrative Order of Consent, groundwater and the Grand River adjacent to Study Area 6 have been monitored since 1983.

Study Area 7, the former "Settling Basin #4," served as a settling basin for Solvay process residues from the soda-ash manufacturing processes at Study Area 1. The basin also received waste pickle liquor and treated effluent from the chromium plant. Titanium-containing acid wastes generated by Electrode Corporation reportedly were also disposed in the settling basins of Study Area 7. The Painesville Township Commissioners formerly operated a municipal landfill in the western part of this Study Area. Another landowner (Joe Berrick, Nacelle Land and Management Corporation and Propane Supply) operated a brine disposal well with two small brine-receiving ponds in this area. Study Area 7 is approximately 520 acres in size. Approximately 60% of Study Area 7 is old field and is vegetated primarily with common reed (*Phragmites australis*). The remaining land is 21% shrub-scrub, 7% mixed old field and shrub-scrub, 7% forested, and 5% maintained.

In contrast to Study Area 4, Study Area 7 is contained by a berm constructed between the Solvay process waste and the Grand River. The berm has been maintained in good condition. Study Area 7 was the last Solvay process waste pond to be used, and has been continuously draining since inputs ceased in the mid-1970s. As of 2001, Study Area 7 contains no standing water, although the lowest part of the basin in the northeast corner contains water-saturated Solvay process waste. These observations suggest that Study Area 7 is still draining.

2.1.3 Aquatic Ecological Resources

The following sections describe the aquatic ecological resources of the Site. Resources are described for the purposes of identifying potential receptors of interest for the Lake Erie and Grand River Baseline ERA. Specific aquatic receptors of interest are selected for evaluation in the Lake Erie and Grand River Baseline ERA in Section 2.2. Additionally, the quality of aquatic resources as evaluated through Ohio EPA, EnviroScience, Inc. and Hull & Associates, Inc. sampling provides a line of evidence in the assessment of risks to aquatic receptors (Section 5). Biological sampling locations, along with surface water and sediment sampling locations, are depicted graphically on Figure 2-20.

2.1.3.1 Aquatic Resources and Use Attainment Data

Data for describing aquatic resources in the Grand River and performing the use attainment analysis were gathered from the following sources:

- *Biological and Water Quality Study of the Grand River: Lake, Ashtabula and Geauga Counties, Ohio* (Ohio EPA, 1987);
- Unpublished data gathered by Ohio EPA in 1988 was obtained from the Ohio EPA's Ecological Assessment Unit (Ohio EPA/EAU); (Ohio EPA, 1988.);
- Unpublished data gathered by Ohio EPA in 1993 was obtained from the Ohio EPA's Ecological Assessment Unit (Ohio EPA/EAU); (Ohio EPA, 1993.);
- *Biological and Sediment Quality Study of the Grand River at the Diamond Shamrock Lagoons Area: Lake County, Ohio* Based on 1994 data, including fish tissue fillet data. (Ohio EPA, 1995);
- *Biological and Water Quality Study of the Grand and Ashtabula River Basins Including Arcola Creek, Cowles Creek, and Conneaut Creek: Ashtabula, Geauga, Lake, and Trumbull Counties* Based on 1995 and previous data. (Ohio EPA, 1997);
- *Aquatic Survey of the Lower Grand River*, Lake County, Painesville, OH. Based on 2000 data. (EnviroScience, Inc., 2001) (Appendix N);
- *Aquatic Survey of the Lower Grand River*, Lake County, Painesville, OH. Based on 2001 data. (EnviroScience, Inc., 2002) (Appendix O); and
- *Assessment of Fish Communities on the Grand River at River Mile 3.5 adjacent to the Former Painesville Works Site, Lake County, OH.* Based on 2002 data. (Hull & Associates, Inc., 2003) (Appendix P).

These data sources are referenced by river mile in Table 2-2.

Biological monitoring is a useful tool for identifying and quantifying impairments in aquatic communities, tentatively identifying or confirming the cause or source of these impairments, and tracking recovery of aquatic biological systems once the cause or source is mitigated. Ohio EPA has developed an extensive state-wide biological monitoring program that seeks to set reasonably attainable biological and habitat goals for different stream and river systems and to track progress toward these goals.

Ohio EPA has identified separate ecoregions within the state that group together streams and rivers with similar geology, stream morphological characteristics and biological communities. The expectations for attainment of various biological and habitat goals vary among ecoregions, but is consistent within ecoregions. Reasonably attainable biological goals (i.e., biocriteria for fish and benthic macroinvertebrates) and habitat goals are identified by intensive study of reference sites within ecoregions, chosen to represent a relatively undisturbed condition.

Biocriteria support the overall goal of aquatic life use attainment. All streams and rivers are assigned one or more beneficial uses in Ohio's Water Quality Standards, including aquatic life uses such as Exceptional Warmwater Habitat, Warmwater Habitat and Modified Warmwater Habitat. Measurements of the biological communities within a given stream are used to calculate metrics (i.e., Index of Biotic Integrity and Modified Index of Well Being for fish, Invertebrate Community Index for benthic macroinvertebrates) that are then compared to ecoregion-appropriate biocriteria to determine whether biocriteria are being met. The degree to which each biocriterion is met is considered together in determining whether the overall aquatic life use is being attained.

This use attainment analysis utilizes all biological and habitat data gathered from 1987 through 2002, information on potential sources of site-related contaminants associated with the Painesville site, and possible non-site related contaminant sources, to examine the potential for causal associations between the site and observed biological impairments in the Grand River reach flowing through the Site.

2.1.3.2 Aquatic Life Use Attainment Methods

Ohio EPA/EAU periodically performs biological monitoring of streams and rivers in support of their biocriteria program, and publishes reports or Technical Support Documents (TSDs) containing their monitoring results. Ohio EPA's methods are documented in the TSDs and in a series of documents developed to support the use of biological criteria by outlining the rationale for using biological information, the methods by which the biocriteria were derived and calculated, the field methods by which sampling must be conducted, and the process for evaluating results (DeShon, 1995; Ohio EPA, 1987a; Ohio EPA, 1987b; Ohio EPA, 1989; Ohio EPA, 1989b; Ohio EPA, 1990; Rankin, 1989; Rankin, 1995; Thoma, 1998; Yoder, 1995; Yoder and Rankin, 1995a; Yoder and Rankin, 1995b; Yoder and Rankin, 1995c).

EnviroScience, Inc. (Enviroscience) gathered data on biological communities and physical habitat in the Grand River in August and October 2000 and in July and August 2001 under contract with SECOR (Okemos, MI). Enviroscience's work was observed by SECOR and Hull, with technical guidance provided by Ohio EPA's Ecological Assessment Unit. With the guidance and approval of Ohio EPA field staff, Enviroscience chose four sampling locations in the Grand River reach within the Painesville Works Site. Two downstream locations (GR-6 at RM 3.5 and GR-5 at RM 3.9) were chosen within the lacustuary zone, defined roughly as the reach of a river from the first riffle to the lake proper. The lacustuary zone is transitional between the lotic (free-flowing) and lacustrine (lake) systems, and Ohio EPA has developed methods and benchmark lacustuary biocriteria that reflect the transitional nature of fish communities located in the lacustuary zone. In general, fish and macroinvertebrate communities within the lacustuary zone are expected to change significantly from those observed in free flowing river segments because the lacustuary represents a transitional zone between lotic and lentic conditions characterized by decreased flow velocities, fluctuating water levels, and changes in channel morphology related to both natural transition and anthropogenic disturbances common to these areas. For this reason, the WWH biocriteria do not apply to lacustuary areas or Lake Erie harbors (see OAC 3745-1-07 Table 7-16). Ohio EPA has developed sampling methodologies and biological indices for the evaluation of the fish community (Thoma, 1998) and macroinvertebrates for lacustuaries, harbors, and Lake Erie near shore areas. However, biological criteria for these areas have not yet been promulgated into the water quality standards. Nevertheless, the analytical methodologies developed for Lake Erie lacustuaries and harbors can be used to analyze resource integrity and are the best tools available for assessing biological community performance.

Two upstream sampling locations (GR-3 at RM 4.7 and GR-2 at RM 5.5) were chosen above the first riffle located at RM 4.6.

Enviroscience's methods for the biological assessment of the four study areas in the Grand River within the Site are detailed in two reports, included herein as Appendix N and Appendix O. All methods used were consistent with Ohio EPA methods, guidelines and field protocols.

Hull & Associates, Inc. (Hull) conducted a quantitative assessment of fish communities at RM 3.5 (GR-6) on October 3, 2002. Verbal site-specific technical guidance was provided by Ohio EPA/EAU. The objective of this study was to determine if fish biocriteria and habitat scores were consistent with previous studies. Dr. Terry Keiser from Ohio Northern University accompanied Hull during the assessment and provided the electrofishing equipment. The fish community assessment was conducted following the methods described in Hull's letter report, included herein as Appendix P. All methods used were consistent with Ohio EPA methods, guidelines and field protocols. Biological index values were calculated by Ohio EPA staff from the Ecological Assessment Unit. Ohio EPA tabulated the fish data collected by Hull and calculated the Index of Biotic Integrity (IBI), Lacustuary Index of Biotic Integrity (LIBI), Modified Index of well being (MIwb) and Lacustuary Index of well being (LMIwb).

Because the interim lacustuary criteria are a fairly recent development, data sets that were gathered in lacustuary areas prior to introduction and fine-tuning of the interim lacustuary criteria must be interpreted with caution. If data collected from a lacustuary zone are compared to the generally higher WWH biocriteria, the result may be a conclusion that the WWH aquatic life use is partially attained or not attained. For this use attainment analysis, Ohio EPA applied the interim lacustuary methods to older data sets to back-calculate appropriate lacustuary biological metrics for these older data sets. Thus these older data sets within the lacustuary zone may be directly compared to the interim lacustuary biocriteria to determine use attainment.

2.1.3.3 Aquatic Life Use Attainment Causal Associations

Ohio EPA interprets the results of biological monitoring data integrating methodologies for the analysis of biological data with other data regarding water resource integrity such as water chemistry, sediment chemistry, and habitat quality (Yoder and Rankin, 1995c). As noted by Ohio EPA, the identification of impairment in streams and rivers is a straightforward matter, while ascribing causes and sources of observed impairment relies on:

> "...interpretation of multiple lines of evidence including water quality data, sediment data, habitat data, effluent data, land use data, and biological results" (Ohio EPA 1997, p. 22).

Identifying causes and sources of observed impairment utilizes a weight-of-evidence approach, and may be inconclusive if sufficient data has not yet been gathered from a particular reach.

2.1.3.4 Aquatic Life Use Attainment Metrics

The Ohio EPA periodically measures fish and invertebrate community quality and physical/ chemical characteristics of Ohio's streams and rivers, primarily to identify changes in water quality over time and to determine the extent to which use designations for each waterway are attained. Comparable data describing aquatic resources in Lake Erie adjacent to the Painesville Site are not available. Indices of fish and invertebrate community quality and physical habitat quality, as well as ancillary water quality data, are described below.

Fish Data for the Use Attainment Evaluation: The Ohio EPA, EnviroScience, Inc., and Hull used electrofishing to assess fish community quality in the Grand River during 1987, 1993, 1994, and 1995 (Ohio EPA),in 2000 and 2001 (EnviroScience, Inc.), and in 2002 (Hull). Fish were identified, counted, weighed, and assessed for physical condition, and the resulting data were evaluated using the Index of Biotic Integrity (IBI), the lacustuary IBI (LIBI), and the Modified Index of Well-Being (MIwb). The IBI indicates fish community quality by incorporating twelve metrics that evaluate overall abundance, species richness, tolerant and intolerant taxa, trophic and spawning guilds, and individual fish condition. The MIwb indicates fish community quality more simply, through the incorporation of measured richness of nontolerant species, biomass, and abundance of fish.

Criteria for these indices have been developed for different use designations based on data from numerous reference streams in Ohio. As described in Section 2.1.3.1, three use designations apply to the Grand River upstream of and adjacent to the Site: Exceptional Warmwater Habitat, Warmwater Habitat, and Lake Erie estuary and harbor area (lacustuary). Exceptional Warmwater Habitat is characterized by a high diversity of species and species that are intolerant of anthropogenic disturbance and/or rare, threatened, or endangered. Warmwater Habitat is more typical of the assemblages of aquatic organisms found in free-flowing rivers and streams in Ohio. The Lake Erie estuary and harbor or lacustuary designation reflects the influence of Lake Erie on its tributaries, where decreased water flow rates and decreased physical habitat complexity tend to limit the number and types of aquatic organisms that can be expected. IBI criteria applicable to the Grand River are 48 (Exceptional Warmwater Habitat), 40 (Warmwater Habitat), and 42 (lacustuary) (Ohio EPA, 1995; 1997; Thoma, 1998). Departures of 4 units or less from the IBI criteria are considered non-significant (Ohio EPA, 1995; 1997), *i.e.*, the use designation is attained if the observed IBI index is $\geq$44 (Exceptional Warmwater Habitat), $\geq$36 (Warmwater Habitat), or $\geq$38 (lacustuary) (Ohio EPA, 1995; 1997). MIwb criteria are 9.6 (Exceptional Warmwater Habitat), 8.7 (Warmwater Habitat), and 8.6 (lacustuary). Departures of 0.5 units or less from the MIwb criteria are considered non-significant (Ohio EPA, 1995; 1997).

Invertebrate Data for Use Attainment Evaluation: The Ohio EPA and EnviroScience, Inc. used artificial substrate samplers and other qualitative collection methods to characterize invertebrate community quality in the Grand River during 1987 and 1994 (Ohio EPA) and 2000 and 2001 (EnviroScience, Inc.). The resulting data were evaluated using the Invertebrate Community Index (ICI), which is calculated from ten metrics evaluating taxa richness and the prevalence of tolerant and intolerant taxa. ICI scores may range from zero to 60. Ohio EPA's criteria for ICI scores are 46 (Exceptional Warmwater Habitat), 34 (Warmwater Habitat), and 22 (Lake Erie harbors) (Ohio EPA, 1995; 1997). Departures of 4 units or less from the ICI criteria are considered non-significant (Ohio EPA, 1995; 1997).

Physical Habitat for Aquatic Data for Use Attainment Evaluation: Physical habitat quality was assessed by the Ohio EPA, EnviroScience Inc. and Hull using the Qualitative Habitat Evaluation Index (QHEI), which is a semiquantitative evaluation of stream substrate, instream cover, channel morphology, riparian zone, and stream gradient information.

2.1.3.5 Aquatic Life Use Attainment Results and Discussion

Physical Habitat for Aquatic Life Evaluation: The Qualitative Habitat Evaluation Index (QHEI) is performed to describe the physical conditions present in and adjacent to streams that affect aquatic habitat quality. QHEI accounts for such factors as stream cover, adjacent land uses, presence of riffles, degree of sedimentation, and many other factors. QHEI is a reliable predictor of the quality of aquatic biological communities that can be supported by a given reach of a stream. QHEI is used to determine whether habitat may be a limiting factor for the quality of fish communities. In free flowing streams, QHEI scores greater than 60 are generally conducive to the attainment of the WWH biocriteria for fish (Rankin, 1995a), while QHEI scores below 45 generally indicate habitat limitations that cannot attain these biocriteria.

Ohio EPA performed QHEI as part of its sampling activities in the Grand River in 1987, 1994 and 1995. EnviroScience, Inc. performed the Qualitative Habitat Evaluation Index (QHEI) on areas of the river adjacent to biological sampling areas GR-2, GR-3, GR-5 and GR-6 in 2000

'A review of the QHEI sheets and a comparison to historical QHEI data generated by Ohio EPA indicates that the habitat evaluations were not scored properly and that the scores generated were elevated beyond what could be expected as a reasonable error between observers. Metrics which should be reviewed and re-scored include the cover metric and the riparian zone and floodplain metric.' (Attachment A, Section 6.4.2.B.)

The PRP Group is planning additional field work with Ohio EPA in Spring 2003 to rescore the QHEI through the project site. Mr. Anderson will be assisting with the rescoring and he has stated that it is not expected to change the conclusions of the RI with respect to stresses to the Grand River ecosystem. This additional QHEI data will be submitted to Ohio EPA as supplemental information to the RI, and the review and approval of the RI need not be delayed for lack of this supplemental QHEI data.

Macroinvertebrates Evaluation: The Invertebrate Community Index (ICI) is a metric developed by Ohio EPA to characterize the diversity and quality of benthic macroinvertebrate communities in streams and rivers.

Ohio EPA performed the ICI during sampling activities at various locations on the Grand River in 1987, 1988, 1993, 1994 and 1995. EnviroScience performed the ICI in 2000 and 2001 in four sampling areas adjacent to the Site (GR-2, GR-3, GR-5 and GR-6). The ICI results are summarized in Figure 2-4.

With the exception of the 1987 Ohio EPA sampling effort, results for the ICI were generally poor to fair at and below RM 3.5 and fell below the interim lacustuary criterion for ICI (22). With the exception of lower ICI scores observed by Ohio EPA in 1994 and 1988, ICI met applicable criteria above RM 3.5 for all sampling years throughout the Grand River reach through the Site.

Invertebrate taxa collected in the Grand River adjacent to the Site in 2000 and 2001 are summarized in Table 2-4. The species collected represent a diversity of species and functional groups. These taxa include several families of mayflies (Ephemeroptera), stoneflies (Plecoptera), and caddisflies (Trichoptera), which are generally considered intolerant of anthropogenic disturbance.

A summary and narrative evaluation of the benthic macroinvertebrate data collected at or near the Site for all years is shown in Table 2-5.

Fish Community Evaluation: Two metrics have been developed by Ohio EPA to describe the diversity, quality and overall health of fish communities in rivers and streams. The Index of Biotic Integrity (IBI) is calculated using a series of metrics that take into consideration the types of fish species present and how many individuals of each species are collected in the sampling zone. The Modified Index of Well-Being (MIwb) is calculated in a manner similar to the IBI, but takes into consideration the total mass of each species collected and the presence of gross deformities, erosions, lesions and/or tumors (DELT anomalies).

Ohio EPA performed the IBI at various locations along the Grand River in 1987, 1988, 1993, 1994 and 1995. EnviroScience, Inc. performed the IBI at biological sampling areas GR-2, GR-3, GR-5 and GR-6 in 2000 and 2001. Hull performed the IBI at biological sampling area GR-6 in 2002. The IBI results are presented in Figure 2-5.

IBI scores collected during and after 1994 did not meet the benchmark criterion within the lacustuary area of the site (RM 2.4 to RM 4.7). IBI data collected in 2000, 2001, and 2002 showed the lowest metric value at RM 3.5 (GR6). Above RM 4.7, IBI data collected for all sampling years generally met applicable biocriteria with a few exceptions (see Figure 2-5).

Ohio EPA performed the MIwb at various locations along the Grand River in 1987, 1988, 1993, 1994 and 1995. EnviroScience, Inc. performed the MIwb at biological sampling areas GR-2, GR-3, GR-5 and GR-6 in 2000 and 2001. Hull performed the MIwb at biological sampling area GR-6 in 2002. The MIwb results are presented in Figure 2-6.

MIwb scores decreased from upstream to downstream through the project area, an observation generally consistent with declining habitat quality. However, comparisons of MIwb scores within and among sampling years reveal variable patterns Low MIwb and IBI scores for the fish communities at RM 3.5 (GR-6) in 2000 and 2001, combined with the low ICI scores at the same location, resulted in non-attainment of the WWH aquatic life use designation at this location in both 2000 and 2001. Hull's 2002 data at RM 3.5 (GR-6) also resulted in non-attainment due to a poor IBI score, although the Miwb score was in attainment. The absence of fish at GR-6 noted by EnviroScience in 2001 cannot be explained on the basis of habitat characteristics alone, although QHEI scores were relatively low for this portion of the river. Note that the fish data set collected by Enviroscience, Inc. on August 16, 2001 at GR-6 (RM 3.5) was deleted as directed by Paul Anderson of Ohio EPA. The reason given by Ohio EPA for the deletion is that the lack of fish was likely due to the higher than normal conductivity readings measured in the Grand River at that location on that day (2,081 uhmos) which can occur at lacustuary sites where there is a conductivity source upstream (i.e., from the Site) and downstream (i.e., from the Painesville WWTP).Under these conditions, one can get a zone of stagnation within which a plume of conductivity lies, causing fish to temporarily avoid the area. Therefore, the data was deleted as not representative. The result of this data deletion is that the IBI, LIBI, MIwb, and LMIwb values for 2001 reflect the July 2001 sampling set only, and not an average of the July and August sampling events as would normally be presented.

Fish species collected in the Grand River adjacent to the Painesville Site are listed in Table 2-6. A total of 62 species have been collected in the study area, including a variety of trophic groups and several pollution-intolerant species (*e.g.*, black redhorse [*Moxostoma duquesnei*], silver shiner [*Notropis photogenis*], and brindled madtom [*Noturus miurus*]).

A summary and narrative evaluation of the fish data collected at or near the Painesville Site for all years is shown in Table 2-7.

2.1.3.6 Aquatic Life Use Attainment Summary

The Grand River within the Painesville site has a long history of full attainment of the WWH use between RM 4.2 and the upstream site boundary at RM 5.5 (Table 2-8). In both 2000 and 2001, the upstream sampling locations (RM 4.7 and RM 5.5) were in full attainment of the WWH use designation. Below RM 4.2 to the project boundary at RM 2.4, the Grand River has partially or fully attained its use designation, with the exception of RM 3.5 in 2000, 2001, and 2002 which was in non-attainment.

Three consecutive years of nonattainment at RM 3.5 point to a pattern of water quality degradation at this location. Fish community results were particularly low at this location in 2002 (Hull data), and in Round 2 of the 2001 sampling effort, because Enviroscience found no fish at all. This resulted in a lacustuary IBI of 8 (very poor) and a lacustuary MIwb of 0 (very poor). In both sampling Rounds in 2000 and in Round 1 of 2001, lacustuary IBI results at RM 3.5 ranged from poor to fair.

The aquatic community degradation observed at RM 3.5 in 2000, 2001, and 2002 could potentially be attributed to a number of possible causes including pollutant stressors such as hexavalent chromium and TDS, lacustuary effects, habitat quality and changes, and measurement error. QHEI values at this location suggest that attainment of WWH should be possible, so habitat quality is not likely the sole cause of nonattainment at this location. On the occasion when Enviroscience failed to obtain fish from GR-6, they verified operation of their equipment and reshocked with the same result, so measurement error is not likely.

Pollutant or water quality effects are also a possible explanation for nonattainment at GR-6 in 2000,2001, and 2002. As discussed in Section 2.1.3.3, causal associations between a site or a given pollutant source and observed effects on aquatic communities must be made on a weight-of-evidence basis and with considerable caution. On the basis of the available biological data, it is reasonable to conclude that the impacts to the biological community observed at RM 3.5 are a real phenomenon. Specific pollutant sources to the Grand River are examined in detail in Section 2.3.

The biological sampling results from 2000-2002 taken together suggest that stressors such as water quality, lake levels, or other phenomena make it difficult for a resident, well-balanced fish community capable of meeting ecoregional biological criteria to become established in the upper lacustuary portion of the Grand River near RM 3.5. No single cause is evident for the River's not meeting promulgated biocriteria. However, exceedences of the water quality standards for Cr (VI) and TDS are potentially major factors which cannot be discounted as a cause for the observed instances of partial and non-attainment of the biological criteria observed in the Grand River.

2.1.4 Fish Tissue

Data on fish tissue concentrations of various chemical constituents is reported for the Grand River reach within the Painesville site from three sources:

- Ohio EPA (Quanterra), 1998. This analytical report presents the results of analyses conducted on fish fillets from six species collected by Ohio EPA between RM 2.2 and RM 6.0 in September 1997. Parameters included semivolatile organic compounds (SVOCs) and metals.

- Ohio EPA, 1995. This Technical Support Document contains the results of analyses conducted on fish fillets from four species collected between RM 3.2 and 4.6 in 1994. Parameters included SVOCs.

- Ohio EPA,1998 data. These unpublished results contain analyses conducted on whole body samples of three fish species collected by Ohio EPA between RM 3.5 and RM 4.6. Parameters measured were whole body concentrations (WBCs) of SVOCs.

The fish tissue data sets identified above are in some ways problematic. It is difficult to identify sources of chemicals in fish tissue, particularly for migrating species such as bass, trout and walleye, which are the primary sport fish caught from the river. Hence, there is a great deal of uncertainty as to whether any constituents measured in fish tissue from the fish collected in the Grand River (which included bass) are in fact Site-related. The fish tissue data from the 1998 Ohio EPA sampling event were whole body samples, and not the fillet samples most appropriate for the evaluation of human fish consumption. The results from the Ohio EPA (Quanterra) 1998 study are suspect due to the reported detection of hexavalent chromium in fish tissue; hexavalent chromium is not expected to be found in the reducing conditions nearly universal in animal tissues (Barnhart, 1997).

Any attempt to directly measure Site-related chemical concentrations in Grand River fish tissue would require the development of a sampling plan with Data Quality Objectives developed specifically for that purpose. This was not done for the available data. The determination of fish tissue concentrations from Grand River fish was not part of the Ohio EPA-approved Phase I or Phase II RI Work Plans. At a meeting held with Ohio EPA on September 24, 2002 and in subsequent telephone calls with the Ohio EPA Division of Surface Water, Ohio EPA staff indicated that they have been unable to find quality assurance/quality control (QA/QC) information including laboratory QA/QC, field sampling SOPs or chain of custody documentation for the fish and mussel analyses. In addition, Document #24 (Guidance for Data Usability in Risk Assessment) listed in Appendix B of the Director's Final Findings and Orders (DFFO) specifies the minimum requirements that must be met before data can be used for baseline risk assessment. Ohio EPA agreed that, based on the missing QA/QC information, it is not possible to determine if the fish tissue, whole body and mussel data meet the minimum criteria for data usability. Therefore, fish tissue samples are not used to evaluate site-related risk through the fish ingestion pathway. While the fish tissue data from the three sources listed above cannot be used to answer risk-related questions about the Site, they may be useful in other contexts (*e.g.*, Ohio Health Department considerations). Therefore, the fish tissue data from the three sources described above are qualitatively summarized in Appendix F to this Lake Erie and Grand River Baseline ERA. The attachment includes a discussion of the reported PCB and hexavalent chromium concentrations in fish tissue.

2.1.5 Terrestrial Resources

The following sections describe the terrestrial ecological resources of the Site. Resources are described for the purposes of identifying potential receptors of interest for the Lake Erie and Grand River Baseline ERA. Specific terrestrial receptors of interest are selected for evaluation in the Lake Erie and Grand River Baseline ERA in Section 2.2.

Site-specific data describing ecological resources in the terrestrial study areas of the Painesville Site are limited to the qualitative field reconnaissance data collected for this Lake Erie and Grand River Baseline ERA (Section 2.1), which focused primarily on vegetation types. Flora are discussed in relation to their role as habitat for aquatic-feeding terrestrial animals. Fauna observed or expected to occur in these study areas that may utilize the water resources of the Site are briefly described below.

Flora: A list of plant species observed at the Painesville Site during the qualitative field reconnaissance (October 23-24, 1997) is presented in Table 2-9. Eighteen tree species, nine species of shrubs and vines, and 29 herbaceous plant species were identified. Community types are described in Section 2.1.1. Vegetation at the site appeared to be healthy (normal plant structures, no visual evidence of stress). The predominance of the stress-tolerant common reed (*Phragmites australis*) in Study Area 7 may reflect high moisture, low nutrient levels, and high pH associated with Solvay process residues, as well as the invasive and persistent nature of this species once it has become established in a given area (see discussion of soil quality, below). With the exception of natural successional changes, existing plant communities in the terrestrial study areas would be expected to remain generally similar into the future, in the absence of redevelopment of the site.

Birds: The vegetative communities present at the Painesville Site are expected to provide food, cover, and reproductive habitat for a number of different bird species. Birds may be present any time of year but are most diverse and abundant during the spring, summer, and fall, during migration and breeding (Kricher and Morrison, 1988). The vegetative communities at the site likely host both permanent residents and migrants, as well as winter visitors whose populations vary from year to year (Kricher and Morrison, 1988). It is expected that the site could provide habitat to support feeding, cover, or reproduction for species such as the American robin (*Turdus migratorius*), sparrows (various genera), various songbirds (*e.g.*, the family Emberizidae), American woodcock (*Scolopax minor*), killdeer (*Charadrius vociferus*), eastern meadowlark (*Sturnella magna*), belted kingfisher (*Ceryle alcyon*), Canada geese (*Branta canadensis*), and various raptors (predatory birds) such as red-tailed hawk (*Buteo jamaicensis*) and American kestrel (*Falco sparverius*).

Mammals: The vegetative communities present at the Painesville Site are also likely to be able to support several mammalian species. It is likely that the site could provide habitat for foraging, cover, or reproduction to various rodents, shrews, rabbits, raccoon (*Procyon lotor*), muskrat (*Ondatra zibethica*), mink (*Mustela vison*), and white-tailed deer (*Odocoileus virginianus*), mammals which are generally found throughout northeast Ohio.

Reptiles and Amphibians: The variety of land cover types present at the Painesville Site might support reptiles and amphibians, including snakes, turtles, toads, frogs, and salamanders. Examples of regionally common reptiles include black rat snakes (*Elaphe obsoleta obsoleta*), northern water snakes (*Nerodia sipedon*), shorthead garter snakes (*Thamnophis brachystoma*), snapping turtles (*Chelydra serpentina serpentina*), and painted turtles (*Chrysemys picta*). Examples of regionally common amphibians include American toads (*Bufo americanus americanus*), northern spring peepers (*Hyla crucifer crucifer*), leopard frogs (*Rana pipiens*), bullfrogs (*Rana clamitans*), spotted salamanders (*Ambystoma maculatum*), and red-spotted newts (*Notophthalmus viridescens viridescens*).

Soil Quality Characteristics: Physicochemical measurements of soil quality characteristics at the Site have included total organic carbon content, moisture content, and pH (Table 2-10). Relatively low organic carbon levels (<1%) are reported throughout the site. Organic matter serves as an important source of nutrients in soil; thus, it can be inferred that soils at the Painesville Site are probably nutrient-poor. Soil moisture content generally averages approximately 15% but is higher in the former Solvay process residue settling basins, particularly in portions of Study Area 7 where the average moisture content is approximately 40%.

Measured pH levels in the terrestrial study areas range from 3.6 to 12.3 (Table 2-10). Soil pHs falling outside a range of about 5 to 10 can limit the growth of many species. In Study Areas 1, 3 and 4, pH levels generally fall within this range, but Study Areas 2 and 5 contained pH observations less than 5 and Study Area 7 contained pH observations greater than 10. The locations where these elevated pH values were measured are generally clustered toward the center of Study Area 7, and vegetation in this area was observed to be sparse during the qualitative field reconnaissance.

2.1.5.1 Rare, Endangered and Threatened Species

The United States Fish and Wildlife Service (USFWS) and the Ohio Department of Natural Resources (ODNR) were contacted regarding the potential presence of sensitive ecological receptors at or near the Painesville Site (Appendix B). Sensitive ecological receptors include, but are not limited to, federal- and state-recognized threatened and endangered species, state-listed species of concern, and critical fish and wildlife habitat.

The USFWS identified three species potentially present within the vicinity of the Painesville Site and protected by the federal Endangered Species Act. These include the endangered Indiana bat (*Myotis sodalis*), the threatened bald eagle (*Haliaeetus leucocephalus*), and the endangered piping plover (*Charadrius melodus*). Habitat conditions necessary to support breeding populations of these species have not been observed anywhere on the Painesville Site, although transient individuals are a possibility. The ODNR identified three species listed in the Natural Heritage Inventory: the river redhorse (*Moxostoma carinatum*; a "special interest" fish), the bigeye chub (*Notropis amblops*; listed by the ODNR but not by the Ohio Division of Wildlife), and the upland sandpiper (*Bartramia longicauda*; threatened). The ODNR did not identify existing or proposed state nature preserves or scenic rivers within the site boundaries. Additionally, the ODNR did not report any unique ecological sites, geological features, champion trees, or state parks, forests, or wildlife areas within the site boundaries.

Persistent, Bioaccumulative and Toxic (PBT) compounds are of particular concern when considering potential impacts on potential RTE populations. In this ecological risk assessment, the Toxicity Reference Values (TRVs) used are protective of any RTE species potentially present at the Site. For a more detailed discussion of how the TRVs in this ecological risk assessment were derived so as to be protective of RTE populations, please see Section 4.3.2.7.

2.2 Receptors of Interest (ROIs)

Receptors of interest (ROIs) are selected to represent the organisms that might be present at the Painesville Site, because it is not feasible to complete a risk assessment for each species. The ROI selection process and the specific receptors chosen for the Lake Erie and Grand River Baseline ERA are described in the following subsections.

2.2.1 ROI Selection Process

The ROI selection process is consistent with SECOR (1997) and U.S. EPA guidance (1992; 1994a; 1995a; 1997a). Selection of ROIs is based on two primary considerations: (1) the occurrence of potentially complete pathways for exposure of ecological resources at the site to chemicals in environmental media, and (2) the feasibility of completing a quantitative assessment for the identified pathways. The exposure pathways examined include:

- Direct contact with sediment or surface water;
- Ingestion of sediment or surface water; and
- Ingestion of chemicals via the food web.

Groundwater is not directly contacted by receptors and is not part of a direct, complete exposure pathway. Additionally, exposures via inhalation are considered insignificant and are not evaluated.

The evaluation of potential exposure pathways is summarized in Figure 2-7A and Figure 2-7B. Some pathways, although complete, would be impossible to evaluate in the Lake Erie and Grand River Baseline ERA due to the absence of toxicological information. Toxicological data are not available for reptiles and amphibians, and effects on these receptors therefore cannot be assessed. Key exposure pathways are assessed for the remaining ecological resources described in Section 2.1.3. The ROIs selected to represent these ecological resources are described below.

2.2.2 Aquatic ROIs

Selection criteria for aquatic ROIs include three factors specified in U.S. EPA guidance (1989a; 1992; 1997a) for determining "key organisms" in an aquatic food web: (1) resident communities or species exposed to the highest concentrations of chemicals in sediment and surface water; (2) species or functional groups considered to be essential to, or indicative of, the normal functioning of the affected habitat; and (3) threatened or endangered species (according to federal or state definitions).

Aquatic ROIs are identified for the Grand River and Lake Erie. The remaining study areas do not support habitat for aquatic biota. Aquatic ROIs selected for the Lake Erie and Grand River Baseline ERA include benthic invertebrates, and fish and aquatic invertebrates and aquatic plants.

Benthic Invertebrates: Benthic invertebrates live in sediment and feed on detritus or other organisms in the sediment. As such, they are directly exposed to the highest concentrations of chemicals in sediment. Benthic invertebrates are significant primary consumers in many freshwater systems and are prey species for some species of resident fish, amphibians, birds and mammals.

Fish and Aquatic Invertebrates: Fish and aquatic invertebrates live in the water column and are directly exposed to the highest concentrations of chemicals in water. Fish and aquatic invertebrates serve as primary and secondary consumers and as prey species for higher-trophic-level organisms. Several fish species present in the region of the Painesville Site are important to recreational fishing.

Aquatic Plants: Aquatic plants include both vascular plants and nonvascular plants (e.g., algae). Vascular plants may be partially or entirely exposed directly to the highest concentrations of chemicals in water depending upon whether their growth form is emergent or submergent, respectively. While algae occur throughout the water column of rivers and lakes, rooted vascular plants tend to occur at the margins of these water bodies. Plants serve as the primary producers in nearly all food webs worldwide. Rooted aquatic vascular plants are rare at the margins of the Grand River and Lake Erie at the Site, but algae are assumed to be common as they are in most rivers and lakes.

2.2.3 Wildlife ROIs

In contrast to aquatic ROIs, exposure assessment methods for terrestrial wildlife require the selection of individual species to represent larger trophic groups. Selection of particular wildlife species as ROIs is based on the presence of suitable habitat, expected presence based on range maps, representation of relevant trophic groups (e.g., piscivores and invertivores), and availability of exposure data. Terrestrial wildlife ROIs selected to characterize aquatic exposures are evaluated for the Grand River and Lake Erie.

Two species of birds and two species of mammals are selected as ROIs for the Lake Erie and Grand River Baseline ERA, including the belted kingfisher (*Ceryle alcyon*) and the mink (*Mustela vison*) as piscivores, and the spotted sandpiper (*Actitis macularia*) and the raccoon (*Procyon lotor*) as aquatic invertivores. Exposure information is readily available for each of these species. The wildlife ROIs for the Painesville Site are described as follows:

> **Spotted sandpiper:** The spotted sandpiper represents aquatic invertivorous birds, such as shorebirds and waterfowl. This species is expected to feed on sediment organisms and have extensive contact with sediment. The spotted sandpiper has a relatively small home range and body size and is expected to experience greater exposure to COIs than larger invertivorous birds.
>
> **Raccoon:** The raccoon represents aquatic invertivorous mammals. In general, mammals do not feed exclusively on aquatic and benthic invertebrates. However, it is possible that the raccoon could feed primarily on invertebrates (U.S. EPA, 1993b), and an exclusively invertivorous diet is assumed for the Lake Erie and Grand River Baseline ERA. In addition to diet, chemical exposure may occur through ingestion of water and sediment, because raccoons commonly wash food items in water.
>
> **Belted kingfisher:** The belted kingfisher represents piscivorous birds. This species feeds primarily on fish, which it captures by diving into the water.
>
> **Mink:** The mink represents piscivorous mammals. The mink is a top-level carnivore that feeds almost exclusively on fish, small mammals, birds, eggs, frogs, and macroinvertebrates. Mink have been shown to have a heightened sensitivity to some chemicals (Bleavins *et al.*, 1984; Rush *et al.*, 1983) and are thereby a sensitive (to chemical stressors) mammalian receptor.

2.3 Pollutant Inputs to The Grand River

A full analysis of aquatic life use attainment in the Grand River in the context of problem formulation requires discussion of the sources of pollutants that could potentially affect aquatic life. This discussion is provided in the following sections.

2.3.1 Chemical inputs from groundwater

Chemicals detected in groundwater on the Site may enter the Grand River and represent a risk to ecological receptors. U.S. EPA's BIOSCREEN model version 4.1 (July, 1997) was used to evaluate chemicals in groundwater migrating to the Grand River. A groundwater chemical of interest (COI) list was developed in cooperation with OEPA and consists of groundwater chemicals exceeding OMZA criteria at the groundwater well locations. Groundwater COIs are as follows:

- Arochlor –1254 and Arochlor –1260
- Arsenic
- Barium
- Benzene
- Benzo(a)pyrene
- Carbon Tetrachloride
- Chloroform
- Chromium VI
- Cyanide
- 4-4'-DDT
- Dieldrin
- Mercury
- Naphthalene
- Pentachlorophenol
- Phenanthrene
- Vanadium
- Vinyl Chloride

Dieldrin was evaluated separately from the quantitative BIOSCREEN model since 1) dieldrin's human health non-drinking water OMZA is 0.0000065 ug/L, far below achievable reporting limits, thus making it impossible to demonstrate compliance using modeling or direct measurement, 2) dieldrin is detected at only four groundwater wells (out of 85 wells) and as "J" estimated values (i.e., below the Practical Quantitation Limit), 3) the Site does not have known past historical uses of dieldrin that would lead to potential sources or source areas on the Site and 4)) on-site soils are not a source of dieldrin to groundwater. Dieldrin is discussed qualitatively in the uncertainty section (Section 5.1.2).

Each maximum detected groundwater concentration in each groundwater well with an OMZA exceedance for that COI was modeled using the distance from that well to either the Grand River or Lake Erie (depending upon the groundwater divide) or to both the Grand River and Lake Erie for the 33 wells identified as being within the "groundwater divide zone" as determined by OEPA. Groundwater from the following 33 wells, located north of Fairport Nursery Rd. within the "groundwater divide zone" were modeled to both Lake Erie and the Grand River:

- SW1-2
- SW1-1
- SW1-3
- P1B1-01

- SW1-7
- MW-1B1-08
- MW-1B1-06
- MW-1B1-05
- MW1B1-04
- MW-1B1-03
- MW-1B1-02
- SW1-4
- ASR-MW8
- ASR-MW1
- ASR-MW2
- ASR-MW5
- CL1-1/MW-7
- ASR-MW3
- MWB-1
- MWB-5
- ASR-MW4
- SW1-5
- SW1-10
- SW3-4
- SW1-8
- MW-40
- MW-49
- MWB-2
- MW-47
- MWB-6
- SW1-12
- MWB-4
- SW1-6

The BIOSCREEN model inputs and assumptions were discussed and agreed upon with OEPA at a meeting held on March 19, 2003. The hydrogeology, dispersion, adsorption, biodegradation, general inputs, and source area input assumptions are summarized in Table 1 of Appendix I. Inputs and assumptions specific to each chemical and monitoring well location are summarized in Table 2 of Appendix I. Model predicted groundwater concentrations at the point of discharge to either Lake Erie or the Grand River or both (e.g. depending upon the groundwater divide zone) are compared to OMZA water quality criteria in Tables 3-18 of Appendix I.

Model predicted concentrations at the point of discharge to the Grand River exceed the OMZA surface water quality standards for the protection of aquatic life or wildlife for six chemicals (arsenic, barium, cyanide, chromium VI, mercury, and vanadium).

Based on these results, Ohio EPA requested, in a letter dated April 16, 2003, that either 1) the remainder of the metals and chlorinated solvents, (not yet modeled), be modeled to determine the complete list of metals and chlorinated solvents to be evaluated further or 2) conclude that all metals and chlorinated solvents require further evaluation. Based on Ohio EPA's recommendations, the remainder of the metals and chlorinated solvents exceeding OMZA standards within the groundwater wells were modeled. These results are presented in Tables 19-30 of Appendix and summarized below:

Model predicted concentrations at the point of discharge to the Grand River exceed the OMZA surface water quality standards for the following additional metals and additional chlorinated solvents: antimony, copper, and selenium. A summary of the chemicals with BIOSCREEN model predicted concentrations at the point of discharge to the Grand River exceeding OMZA surface water quality standards by Study Area is provided below. :

Study Area	Parcel ID	Model Predicted Concentrations Exceed OMZA at the Point of Discharge to Grand River
Study Area #1		
Study Area #2		
Study Area #3		
Study Area #4		
Cyanide	4B2	X (Aq. Life only)
Study Area #5		
Study Area	Parcel ID	Model Predicted Concentrations Exceed OMZA at the Point of Discharge to Grand River
Cyanide	5B1	X (Aq. Life only)
Study Area #6		
Antimony	6B1	X (Aq. Life & HH)
Arsenic	6B1	X (Aq. Life only)
Copper	6B1	X (Aq. Life only)
Cyanide	6B1	X (Aq. Life only)
Chromium VI	6B1	X (Aq. Life & HH)
Selenium	6B1	X (Aq. Life only)
Vanadium	6B1	X (Aq. Life only)

Study Area #7		
Barium	7C1/7B1	X (Aq. Life only)
Mercury	7B1 and 7C1	X (HH & Wildlife)

HH = OMZA for the protection of human health via non-drinking water (i.e. fish ingestion).

Aq. Life = OMZA for the protection of aquatic life.

Wildlife = OMZA for the protection of wildlife

Groundwater chemicals with model predicted concentrations that exceed OMZA surface water quality standards at the point of discharge to the Grand River may pose a potential risk to aquatic life or wildlife pathways and will be evaluated further in the Feasibility Study (FS) portion of the project.

Elevated concentrations of Cr (VI) in groundwater between Study Area 6 and the Grand River have been detected, and the modeling results predict that exceedances of the OMZA standard for total chromium and Cr (VI) in the Grand River could be substantial, exceeding the OMZA criterion for Cr (VI) (11 ug/L) by more than 55,900fold (Appendix I Table 15)However, detected exceedances of the OMZA standard for Cr (VI) in the Grand River were much less substantial than predicted by modeling. The conservative assumptions required of the BIOSCREEN model, result in some cases in unrealistic predictions. Specifically, the assumption of a nondepleting source that remains active for 100 years coupled with assuming no biodegradation result in over estimated of predicted concentrations. In 2000 and 2001, there were 46 exceedances of the OMZA standard for Cr (VI). Of these exceedances, the maximum detected concentration was 21 times the OMZA standard, while the great majority of exceedances (38) were two times the OMZA standard or less.

It should be noted that the water sampling program in the Grand River (as described in the Phase II Work Plan, SECOR, 1999) did not attempt to physically locate points of contact between groundwater and surface water in the Grand River. However, the program did involve collecting water samples near the river bottom (in addition to the middle and top of the water column) at each of seven equally-spaced sampling points across the width of the river at each of the seven sampling stations (GR-1 through GR-7). This design represents a reasonable attempt to collect Cr (VI) concentration data at the groundwater-surface water interface and throughout the water column, and can be relied upon to adequately characterize the concentration and distribution of hexavalent chromium in the Grand River through the Site for the purposes of this Ecological Risk Assessment. However, this design cannot be relied on to detect all hexavalent chromium concentration maxima that may have occurred at all points during the entire Phase II study period. It is possible that a different sampling design implemented at a different time could produce different results.

One explanation for the observation that OMZA exceedances of the Cr (VI) standard are much lower in magnitude than predicted by modeling is that hexavalent chromium or Cr (VI) is reduced to Cr (III) within the ranges of oxidation/reduction potential (ORP) and pH typical of the soil and groundwater at the Site. Figure 2-8, and Figures 2-9 and 2-10 are scatter plots of oxidation-reduction potential (ORP) vs. pH for groundwater and soils zero to four feet and four to ten feet, respectively, and constitute phase diagrams for the oxidation state of chromium in these media. ORP and pH conditions conducive to the existence of Cr (VI) were found in only four soil samples from two soil borings at zero to four feet in Northern Study Area 4 and in no groundwater samples. These phase diagrams suggest that reducing conditions are present across the Painesville Site. These reducing conditions probably work to minimize the amount of Cr (VI) entering the river system from the COPR landfill.

In addition to redox conditions, the effect of water chemistry (pH, competing ions, complexing agents) and of natural solids (adsorbents) is important in the chromium hydrogeochemical cycle. Two main mechanisms are believed to control the mobility of hexavalent chromium: Cr(VI) reduction into Cr(III) which is afterwards rapidly precipitated or adsorbed, and adsorption (Rai et al., 1988). Cr (VI) is also readily reduced to Cr (III) in the presence of organic matter (Richard and Bourg, 1991).

There may be other physical and chemical processes that influence the speciation of Cr at work at this Site not discussed in this text, although it is likely that the reduction process is the primary physical/chemical process affecting the speciation of Cr at the site. The reduction of Cr (VI) may be the best available explanation for the detected Cr (VI) concentrations in the Grand River being low compared to the elevated Cr (VI) concentrations observed in groundwater adjacent to the COPR landfill several hundred feet from the river. The difficulty of precisely measuring the chromium at the point(s) of contact between groundwater and the Grand River may be another explanation for the differential concentrations observed.

Whether Cr (VI) is entering the Grand River directly from groundwater or indirectly via oxidation reactions in sediment, Cr (VI) may be relatively stable once in surface water assuming relatively low concentrations of reducing materials are present (U.S. EPA 1984).

The speciation of Cr is complex, and the oxidation states of Cr in sediments are difficult to predict without empirical measurement of the suite of conditions that can affect Cr speciation. Under conditions of partial equilibrium with atmospheric oxygen, oxidation of Cr(III) to Cr(VI) by oxidizing compounds (e.g., manganese dioxide) can occur in moist soils and sediments (USEPA 2000). At the same time and under the same conditions, Cr (VI) can be reduced to Cr (III) in the presence of manganese oxide and organic acids. The conditions present in sediment (including ORP, pH, presence of organic matter, and relative concentration of the different manganese oxide species) at any given time would control the proportional representation of Cr species present, although these parameters have not been measured for Grand River sediments. Therefore, the potential for Grand River sediments to produce (via *in situ* oxidation) and maintain concentrations of Cr (VI) that could represent a risk to aquatic life cannot be evaluated.

This modeling assessment shows that groundwater from the Painesville Site could contribute to Cr (VI) loading in the Grand River with potential adverse effects on aquatic life. However, the actual Cr (VI) concentrations in the Grand River are much lower than predicted by the model, probably as a result of mechanisms of the type described here for Cr (VI).

2.3.2 Painesville WPCP

The Painesville WPCP (Water Pollution Control Plant) discharges at RM 2.9 within the lacustuary zone. In this transitional zone of the river between true lotic and true lacustrine river environments, river flow is influenced to a degree by Lake Erie water levels. When Lake Erie water levels are high due to various factors such as high water inputs and/or seiche conditions, the Grand River may pool (i.e., cease flowing) throughout the lacustuary zone or even reverse flow up to the pipe bridge at about RM 3.7 (Roger Thoma, Ohio EPA, personal communication). Thus it is possible for the Painesville WPCP discharge to influence water and sediment chemistry to some unknown degree throughout the lacustuary zone up to the first riffle at RM 4.7.

As noted in Section 6.4.1.2 of the RI Phase II Report (SECOR, 2002), the highest loading of TDS of all the eight outfalls sampled was observed at the Painesville WPCP outfall.

Additional outfall discharge monitoring data from the Painesville WPCP was obtained from Ohio EPA for the years 1998-2001. The 50th and 95th percentile concentrations of pH, Cr (VI) and TDS in effluent are shown in Figures 2-11, 2-12 and 2-13, respectively. These figures show that the Painesville WPCP met Ohio EPA surface water quality criteria protective of aquatic life before mixing for pH and TDS, and that the discharge exceeded the promulgated OMZA criterion at the outfall for Cr (VI) (11 ug/L) on several occasions in 1999, 2000 and 2001. After mixing, Cr (VI) discharge from the WPCP is not expected to exceed the promulgated Cr (VI) standard.

These data suggest that the discharge of pH, TDS and Cr (VI) from the Painesville WPCP at RM 2.9 is unlikely to cause, or to contribute in any but a very minor way, to failure to meet chemical or biological water quality criteria within the Site. However, it is possible that interactive effects between releases to the Grand River from the Painesville Works Site and the discharge from the Painesville WPCF exist which may influence biological integrity in the lacustrine portion of the river in ways which have not been quantified through this investigation.

2.3.3 Outfalls

During Phase I investigations at the Painesville site, eight outfalls were identified within the study area. These outfalls, identified as OF-1 through OF-8, were sampled during Phase II sampling operations. The results of this sampling are discussed in Section 6.4.1.2. The outfalls sampled do not appear to have the potential for water quality degradation in the Grand River.

2.3.4 Runoff

Some soil sample locations where PCBs were detected in surface soils (0-4') are in proximity to the Grand River (see Figure 2-21), suggesting a possible source of PCBs to the River via entrainment of contaminated soils by surface runoff. In addition, PCB-contaminated soils located in or near the Grand River floodplain could be eroded and enter the River during flood events. PCBs have not been detected in groundwater anywhere on the Site, minimizing the likelihood of a groundwater route for PCBs to the Grand River. The likelihood that surface runoff or flood erosion events could transport surface soil PCBs to the Grand River was evaluated for soil sample locations adjacent to the Grand River where PCBs were detected.

Prior to the Phase II sampling, either of two PCB compounds (Aroclor 1254 and 1260) was detected at 12 sampling locations at the Site (Appendix C). During the 2000 Phase II sampling, one to three PCB compounds (Aroclor 1248, 1254, and 1260) were detected at 69 locations at the site (Table 2-12 and Appendix C).

Of the 81 locations where PCBs were detected, 74 locations were located more than 1000' from the Grand River (see Figure 2-21), most of them north of Fairport Nursery Road. Although the cutoff distance of 1000 feet for defining the area adjacent to the River is arbitrary, it serves to focus attention on those areas where PCB contamination in soils has the highest potential to reach the Grand River.

At each of the seven sample locations where PCBs were detected in surface soils within 1,000 feet of the Grand River, the vegetative cover type at the location was determined using Figure 2-21. In addition, the plant community type located between each sampling location and the Grand River was determined. Finally, the topography of the area around each sample location was evaluated to determine if the slope and direction of the land surface were conducive to surface runoff to the Grand River. The relative potential (high, medium and low) of each sample location to serve as a source of PCBs to the Grand River via surface runoff or flooding was then determined with a stated rationale. The results of this analysis appear in Table 2-11.

Of all sampling locations where PCBs were detected, sample locations SW5-1 (1800 ug/kg of Aroclor 1260 detected), SB7-17 (detections ranging from 52 ug/kg of Aroclor 1254, to 84 ug/kg of Aroclor 1260 and 100 ug/kg of Aroclor 1248) and SB7-18 (1100 ug/kg of Aroclor 1254 detected) have the most potential to contribute PCBs to the Grand River. Location SW5-1 was determined to have a high relative potential to serve as a source of PCBs to the Grand River due to its location in the floodplain of the River about 100 feet from its edge. There is scrub/shrub vegetation between this location and the river, so contaminants entrained in surface runoff are not likely to reach the Grand River. However, this location is within the floodplain of the Grand River, increasing the likelihood that contaminants from this location could reach the River. Sample locations SB7-17 and SB7-18 were determined to have a medium potential to serve as a source of PCBs to the Grand River due to their proximity to the Grand River floodplain and their location within a drainage swale that outlets to the Grand River floodplain.

Considering patterns of surface slope and vegetative cover at the Painesville Site, it is considered unlikely that any of the other four locations within 1000' of the Grand River could serve as a PCB source via erosion to the Grand River.

A complete pathway to fish from Painesville site soils (e.g., entrained contaminated soils in runoff or flood waters, to the Grand River, to sediment, to benthic macroinvertebrates, to fish) cannot be established. Despite the relative proximity of these seven sample locations to the Grand River, PCBs have never been detected in Grand River sediments (Appendix C). In addition, Ohio EPA fish tissue data obtained from Ohio EPA's STORET files (via Dennis Mishne, Ohio EPA/EAU) and directly from Ohio EPA/NEDO suggest that whole-body fish tissue concentrations of PCBs upstream of the site are higher than those from within the Site. The concentrations of PCBs in a 1987 whole-body sample of black redhorse taken upstream of the site (RM 9.0, Ohio EPA Sample No. 1987-38; PCB-1254=315 ug/kg; PCB-1260=122 ug/kg) exceeded those detected in whole-body tissues of a black redhorse individual collected in 1998 within the Site (RM 3.5; Ohio EPA Sample No. 18100; PCB-1254=129 ug/kg; PCB-1260=111 ug/kg). These limited data suggest the existence of an upstream source of PCBs that would complicate any attempt to conclusively identify the Painesville Works Site as a PCB source.

2.4 Sediment Quality Characteristics

Sediment quality characteristics have been measured in the Grand River and Lake Erie study areas (Table 2-13). In some cases, Solvay-related dissolved solids entering the surface water may result in the formation of precipitates, when specific conditions of alkalinity and pH exist. As a part of its QHEI measurements, Ohio EPA evaluated "substrate quality" in the Grand River at RM 3.2 and 4.6. Substrate characteristics were listed by Ohio EPA as "limestone, tills, and hardpan/soda ash waste."

Among the sediment quality characteristics that have been measured in the Grand River and Lake Erie (Table 2-13), total organic carbon (TOC) content is of particular interest, because organic carbon levels are the primary factor controlling the bioavailability of hydrophobic organic chemicals that may occur in sediment. The reported TOC levels are relatively low, particularly in Lake Erie where the average TOC concentration is approximately 0.4%. Hydrophobic organic chemicals are expected to be more bioavailable in sediments within the Lake Erie study area than in sediments that contain higher TOC levels (see Section 4.1). However, it should be noted that the extent of soft substrate habitat (*i.e.*, sediment) is limited immediately adjacent to the Site in Lake Erie. During the collection of sediment adjacent to Study Areas 1 and 2, samples had to be collected a minimum of approximately 100 feet from the shoreline, because the substrate closer to shore consisted primarily of concrete debris. Sediment could not be collected from Lake Erie adjacent to Study Area 3 because the substrate was too hard to penetrate with sampling devices.

2.5 Chemical Water Quality

A variety of water quality characteristics have been measured in the Grand River adjacent to the Painesville Site. The water quality parameters of greatest interest include pH and total dissolved solids (TDS), which have the potential to be elevated due to the influence of the former Solvay process residue settling basins adjacent to the Grand River, and hexavalent chromium because of the proximity of the COPR landfill to the Grand River.

Water quality samples were taken in the Grand River during the 2000 and 2001 sampling events. The timing of these samples with respect to river flow is depicted in Figures 2-14 and 2-15. All water quality and biological samples was done during non-peak flow periods. However, two sampling events (electrofishing Round 2 in 2000 and water quality sampling Event 3 in 2001) were immediately preceded by higher flow events.

Ohio EPA and USGS pH data from the station at the Rt. 535 bridge (RM 2.3) from 1962 to 1995 (Figure 2-16) show that pH levels downstream of the Painesville site were highly variable through the late 1960s, but that since about 1994, pH levels have become less variable and are in compliance with water quality standards.

Table 2-14 presents TDS measurements collected in the Grand River between 1987 and 2001 during the summer months (July to September), which typically represent periods of low flow and thus higher TDS concentrations. Several measured TDS concentrations have exceeded the Ohio EPA water quality criterion of 1500 mg/L over the 14-year period reflected in Table 2-14. However, during the entire period of Phase II sampling in 2000 and 2001, only a single TDS measurement at RM 4.7 exceeded the water quality standard.

It should be noted that TDS concentrations measured in grab samples from the Grand River are daily measurements, while the applicable water quality standard (1500 mg/l) is an average criterion. Therefore, the TDS standard does not require that this numeric criterion be met at all times.

From upstream to downstream, TDS concentrations increase markedly at approximately RM 4 and then steadily decrease to background levels near the mouth of the river. This trend is illustrated graphically in Figure 2-17. In the portion of the Grand River influenced by the Solvay process waste settling basins, TDS concentrations are considerably more variable than at upstream or downstream locations. The TDS data evaluated in this Lake Erie and Grand River Baseline ERA are provided in full in Appendix A.

In addition to the evaluation of spatial trends, the TDS data can be examined with regard to possible temporal trends. Summer TDS concentrations spanning several years (1964-1994) were obtained from the U.S. Geological Survey station at RM 2.3 downstream of the Lake Erie and Grand River Baseline ERA study area (USGS station 04212200). This data set was combined with TDS data collected in 2000 and 2001 in Figure 2-18. A general trend of decreasing TDS concentration and decreasing variability in TDS concentration over time is evident (Figure 2-18). TDS inputs to the river will presumably continue to occur until Study Area 7 drains completely, but TDS inputs from groundwater sources related to the Painesville Site will continue to decrease. For comparison to the mean concentrations of less than 1500 mg/L in the samples taken since 1986, TDS concentrations in Grand River surface water during facility operations in the early 1960s were on the order of 4200 mg/L, while data available for the mid-1970s show an average summer TDS level of approximately 3000 mg/L.

2.5.1 Exceedences of Water Quality Criteria

All maximum detected concentrations of surface water parameters collected after 1985 within the project area were screened against applicable OMZA chronic water quality criteria (Table 2-15). Maximum detections of three metals (total chromium, hexavalent chromium (filtered), mercury and TDS were above the OMZA standard.

2.5.2 Water quality trends for hexavalent chromium

Figure 2-19 shows that the average Cr (VI) concentration in Grand River surface water in 2000 and 2001 was low upstream of the Site, that Cr (VI) increased sharply beginning at approximately RM 4.2 and peaked at RM 3.9, and that Cr (VI) dropped and leveled off downstream of RM 3.1. This spatial pattern corresponds to the COPR landfill at Study Area 6, suggesting that Study Area 6 is contributing Cr (VI) to the Grand River. Exceedances of the OMZA standard for Cr (VI) (11 ug/L) were of greatest magnitude at RM 3.9 (sampling location GR-5) near the right descending (or northern) bank. This location is immediately adjacent to the COPR landfill in Study Area 6. In addition, analysis of self-monitoring data submitted by the City of Painesville WPCF has found that exceedences of the OMZA for Cr (VI) have been detected in 25% of the grab samples collected downstream of the WPCF outfall, and that the OMZM for Cr (VI) has been exceeded in 11% of the samples collected between 1995 and 2002. There have been few instances of detectable concentrations of Cr (VI) in the Painesville WPCF effluent, indicating that the source of the Cr (VI) in the downstream ambient samples came from upstream of the treatment plant discharge location.

These results from 2000 and 2001 suggest that Study Area 6 is releasing Cr (VI) to the Grand River. These releases resulted in multiple Cr (VI) concentrations in excess of the OMZA surface water standard. As discussed in Section 2.3.1, Cr (VI) is reduced to Cr (III) in the presence of organic matter and reducing metals such as Mn. Because of the generally reducing conditions present within Area 6, it is likely that the exceedances of Cr (VI) in the Grand River are reduced in both frequency and magnitude as compared to what might be expected through casual estimations based upon concentrations of Cr (VI) in soil and groundwater within the site.

Due to the complexity of Cr speciation, and the uncertainties arising from an environmental sampling program that was (by design) spatially and temporally limited, it is not clear whether or to what extent the non-attainment of the aquatic life use designation observed in 2000, 2001 and 2002 at GR-6 (RM 3.5) is attributable to Cr (VI). Non-attainment at RM 3.5 was due to the low fish community metric scores observed at this location; in fact, no fish were collected via electrofishing at RM 3.5 during the second round of sampling in 2001. To further investigate this low performance of the fish community at RM 3.5 in 2001, additional electrofishing was conducted in October 2002. The results of the 2002 electrofishing event indicate that a fish community was present, but that the fish community did not meet the benchmark lacustuary biocriteria for fish communities. The biological sampling results from 2000-2002 taken together suggest that: 1) stressors such as water quality, lake levels, or other phenomena make it difficult for a resident, well-balanced fish community capable of meeting ecoregional biological criteria to become established in the upper lacustuary portion of the Grand River near RM 3.5., and; 2) that no single cause is evident for the River's not meeting promulgated biocriteria in some years.

It should be noted that Cr (VI) concentrations measured in grab samples from the Grand River are daily measurements, while the applicable water quality standard (11 ug/L) is an average. The OMZA Cr (VI) standard is designed to allow for fluctuations in sampling results. It is possible that a different sampling design incorporating 30-day average sampling could produce different data trends for hexavalent chromium.

2.6 Chemical Inputs to Lake Erie

Chemicals detected in groundwater on the Site may enter Lake Erie and represent a risk to ecological receptors. U.S. EPA's BIOSCREEN model version 4.1 (July, 1997) was used to evaluate chemicals in groundwater migrating to Lake Erie. A groundwater chemical of interest (COI) list was developed in cooperation with OEPA and consists of groundwater chemicals exceeding OMZA criteria at the groundwater well locations. Groundwater COIs are as follows:

- Arochlor –1254 and Arochlor –1260
- Arsenic
- Barium
- Benzene
- Benzo(a)pyrene
- Carbon Tetrachloride
- Chloroform
- Chromium VI
- Cyanide
- 4-4'-DDT
- Dieldrin
- Mercury
- Naphthalene
- Pentachlorophenol
- Phenanthrene
- Vanadium
- Vinyl Chloride

Dieldrin was evaluated separately from the quantitative BIOSCREEN model since 1) dieldrin's human health non-drinking water OMZA is 0.0000065 ug/L, far below achievable reporting limits, thus making it impossible to demonstrate compliance using modeling or direct measurement, 2) dieldrin is detected at only four groundwater wells (out of 85 wells) and as "J" estimated values (i.e., below the Practical Quantitation Limit), 3) the Site does not have known past historical uses of dieldrin that would lead to potential sources or source areas on the Site and 4)) on-site soils are not a source of dieldrin to groundwater. Dieldrin is discussed qualitatively in the uncertainty section (Section 5.1.2).

Each maximum detected groundwater concentration in each groundwater well with an OMZA exceedance for that COI was modeled using the distance from that well to either the Grand River or Lake Erie (depending upon the groundwater divide) or to both the Grand River and Lake Erie for the 33 wells identified as being within the "groundwater divide zone" as determined by OEPA. Groundwater from the following 33 wells, located north of Fairport Nursery Rd. within the "groundwater divide zone" were modeled to both Lake Erie and the Grand River:

- SW1-2
- SW1-1
- SW1-3
- P1B1-01
- SW1-7
- MW-1B1-08
- MW-1B1-06
- MW-1B1-05
- MW1B1-04
- MW-1B1-03
- MW-1B1-02
- SW1-4
- ASR-MW8
- ASR-MW1
- ASR-MW2
- ASR-MW5
- CL1-1/MW-7
- ASR-MW3
- MWB-1
- MWB-5
- ASR-MW4
- SW1-5
- SW1-10
- SW3-4
- SW1-8
- MW-40
- MW-49
- MWB-2
- MW-47
- MWB-6
- SW1-12
- MWB-4
- SW1-6

The BIOSCREEN model inputs and assumptions were discussed and agreed upon with OEPA at a meeting held on March 19, 2003. The hydrogeology, dispersion, adsorption, biodegradation, general inputs, and source area input assumptions are summarized in Table 1 of Appendix I. Inputs and assumptions specific to each chemical and monitoring well location are summarized in Table 2 of Appendix I. Model predicted groundwater concentrations at the point of discharge to either Lake Erie or the Grand River or both (e.g. depending upon the groundwater divide zone) are compared to OMZA water quality criteria in Tables 3-18 of Appendix I.

Model predicted concentrations at the point of discharge to Lake Erie exceed the OMZA surface water quality standards for the protection of aquatic life or wildlife for four chemicals (carbon tetrachloride, cyanide, chloroform, and vinyl chloride).

Based on these results, Ohio EPA requested, in a letter dated April 16, 2003, that either 1) the remainder of the metals and chlorinated solvents, (not yet modeled), be modeled to determine the complete list of metals and chlorinated solvents to be evaluated further or 2) conclude that all metals and chlorinated solvents require further evaluation. Based on Ohio EPA's recommendations, the remainder of the metals and chlorinated solvents exceeding OMZA standards within the groundwater wells were modeled. These results are presented in Tables 19-30 of Appendix and summarized below.

Model predicted concentrations at the point of discharge to Lake Erie exceed the OMZA surface water quality standards for the following additional metals and additional chlorinated solvents: antimony, cobalt, 1,1-dichloroethane, methylene chloride, selenium, and silver.

A conference call to discuss Ohio EPA's April 16, 2003 BIOSCREEN comments was held on April 17, 2003. During the April 17, 2003 conference call, Uniroyal representatives raised concerns regarding the modeling results for the chlorinated solvents originating from the Uniroyal parcel(s). They maintain that for a certain area of the Site the BIOSCREEN model was an over-simplified 1-step model that uses a uniform hydraulic gradient from the origin wells to Lake Erie (much lower elevation), which may result in overestimation of predicted concentrations at the point of discharge to Lake Erie. Based on the outcome of this call, the chlorinated solvents were modeled using the less protective 2-step model for the groundwater pathway to the Lake (i.e. to divide the model runs for the pathway to the Lake into two parts 1) the "flat gradient area" near the source wells and 2) "the steep gradient area" near the Lake shoreline) for the chlorinated solvents. The results of the 2-step BIOSCREEN model of the chlorinated solvents in groundwater migrating toward Lake Erie are presented in Tables 32- 37 of Appendix I and are summarized below:

Model predicted concentrations at the point of discharge to Lake Erie exceed the OMZA surface water quality standards for the protection of aquatic life and wildlife using the 2-Step BIOSCREEN model for the following chlorinated solvents: carbon tetrachloride, chloroform, and methylene chloride. The 2-step model eliminated 1,1-dichloroethane, and vinyl chloride for the pathway to the Lake from further consideration as chemicals with predicted concentrations exceeding aquatic life or wildlife OMZAs at the point of discharge. A summary of the chemicals with BIOSCREEN model predicted concentrations at the point of discharge to Lake Erie exceeding OMZA surface water quality standards by Study Area is provided below. :

Study Area	Parcel ID	Model Predicted Concentrations Exceed OMZAs at the Point of Discharge to Lake Erie
Study Area #1		
Antimony	1B2	X (Aq. Life & HH)
Carbon Tetrachloride	1B3	X (Aq. Life & HH)
Chloroform	1B3	X (Aq. Life & HH)
Cobalt	1B1	X (Aq. Life only)
Methylene Chloride	1B3	X (Aq. Life & HH)
Selenium	1B2	X (Aq. Life only)
Silver	3B1	X (Aq. Life only)
Study Area #2		
Cyanide	2C1	X (Aq. Life only)
Study Area #3		
Study Area	Parcel ID	Model Predicted Concentrations Exceed OMZAs at the Point of Discharge to Lake Erie
Study Area #4		
Study Area #5		
Study Area #6		
Study Area #7		

HH = OMZA for the protection of human health via non-drinking water (i.e. fish ingestion).

Aq. Life = OMZA for the protection of aquatic life.

Wildlife = OMZA for the protection of wildlife.

Groundwater chemicals with model predicted concentrations that exceed OMZA surface water quality standards at the point of discharge to Lake Erie may pose a potential risk to aquatic life and will be evaluated further in the Feasibility Study (FS) portion of the project.

2.7 Identification of Chemicals of Interest (COIs)

The extent of chemicals in environmental media at the Painesville Site is described based on analytical data collected during the Phase I and Phase II RI sampling programs and from other sources. The data consists of validated data from the chemical analyses of sediment and surface water from the Grand River, and sediment from Lake Erie. Only data collected after 1985 are used in order to ensure that all data used in the Lake Erie and Grand River Baseline ERA are comparable to the data collected during the Phase I and Phase II RI and are representative of current conditions at the site. Most of the site-related data collected before 1985 are surface water (Grand River) results that may no longer be representative of current conditions. The specific methods and quality assurance/quality control (QA/QC) protocols followed during sample collections for the Phase I and Phase II sampling are described in Appendix E of the *Remedial Investigation/ Feasibility Study Work Plan for the Diamond Shamrock Painesville Works Site* (SECOR, 1997).

2.7.1 Sources of Environmental Data

SECOR collected Phase I sampling data from August 1997 through December 1997, and Phase II sampling data was conducted from September 2000 through August 2001. Lancaster Laboratories analyzed the Phase I and Phase II samples, and Environmental Standards Incorporated validated the data in preparation for use in the Lake Erie and Grand River Baseline ERA. The Phase I and Phase II sampling programs and other data sources are described in the following subsections. Data were provided by SECOR International Incorporated (Okemos, MI), except as noted.

2.7.1.1 Sediment Data

The following data sets are used to characterize chemical concentrations in surface sediments from Lake Erie and the Grand River within the boundaries of the Site:

- *Phase I Remedial Investigation for the Diamond Shamrock Painesville Works Site.* (SECOR, 1999) Four surface sediment samples were collected along the Lake Erie shoreline of Study Areas 1, 2, and 3. These surface sediment samples were analyzed for volatile organic compounds

(VOCs), semivolatile organic compounds (SVOCs), pesticides, polychlorinated biphenyls (PCBs), and metals including hexavalent chromium.

- *Phase II Remedial Investigation for the Diamond Shamrock Painesville Works Site.* (SECOR, 2002) During this investigation, one sediment sample was collected in the Grand River. This sample was analyzed for Vinyl Chloride, as presented in Section 6.3.1.3 of the Phase II RI Report (Main Body).

- *Biological and Sediment Quality Study of the Grand River in the Vicinity of the Diamond Shamrock Waste Lagoons Area* (Ohio EPA, 1995). This data set consists of results from surface sediment (0-6 in) samples collected from RM 2.8 to RM 5.4 in the Grand River (the Grand River study area for this Lake Erie and Grand River Baseline ERA). These sediment samples were analyzed for VOCs, SVOCs, pesticides, PCBs, and metals including hexavalent chromium.

- *U.S. EPA Expanded Site Inspection.* This data set contains results from surface sediment (0-6 in) samples that were collected from the Grand River study area. These samples were analyzed for VOCs, SVOCs, pesticides, PCBs, and metals. These data are not published and were obtained directly from U.S. EPA.

2.7.1.2 Surface Water Data

Results from surface water samples collected from the Grand River between 1985 and 2001 were used in this Lake Erie and Grand River Baseline ERA. Surface water data were not collected from Lake Erie during Phase I RI or Phase II RI sampling, and surface water data have not been collected historically from Lake Erie near the site boundaries. Therefore, surface water COIs for Lake Erie are not identified in this Lake Erie and Grand River Baseline ERA. The Grand River surface water data sets used in this Lake Erie and Grand River Baseline ERA are as follows:

- *Biological and Water Quality Study of the Grand River - Lake, Ashtabula, and Geauga Counties.* (OEPA, 1987). Two surface water samples were collected during this study in 1987 from the Grand River within the boundaries of the Site. These two samples (O-GR2.8 and O-GR3.1) were analyzed for a list of metals and water quality parameters (*e.g.*, nitrates, nitrites, *etc.*) that is broader than the target analyte list specified for surface water in the RI. Several hundred samples collected under the ACO and during the RI are being used to characterize target analytes in the Grand River. The results of these two samples have been accounted for in this large surface water data set. The two samples had no detected concentrations of total chromium and their TDS results have been incorporated into the ecological risk assessment. Results from samples collected in by Ohio EPA 1987, with the exception of TDS and total chromium data, were not used in the baseline ecological risk assessment since the samples were not collected using the protocol approved in the Remedial Investigation Work Plan for the Site.

- *Analytical Data Collected from Sampling of Monitoring Wells in the Painesville Works Site and the Grand River under a U.S. EPA Administrative Order of Consent.* This data set includes results from surface water samples that were collected from locations within the Grand River study area from 1985 to 1996. These samples were analyzed for total chromium and hexavalent chromium. These data were collected by Tierra Solutions Incorporated analyzed by a contract lab, and submitted to U.S. EPA.

- *Total Dissolved Solids Concentrations in the Grand River.* Measured concentrations of TDS in the Grand River collected since 1985 were downloaded from the STORET database maintained by U.S. EPA (http://www.epa.gov/storet/). These data include measurements by the U.S. Geological Survey (USGS) and Ohio EPA. Additional TDS data for the Painesville Site was obtained from the USGS website at http://water.usgs.gov/nwis/qw. TDS data for locations within the Grand River Study Area (RM 2.8-5.4) are included in the COI selection process.

- *A Second Study of Hexavalent Chromium in the Grand River, Ohio* (White, 1989). This data set contains results from surface water samples collected in 1988 from the Grand River. These samples were analyzed for hexavalent chromium.

- *Phase I Remedial Investigation Work Plan for the Painesville Works Site.* (SECOR,1997). The Phase I RI Workplan did not outline a Grand River surface water sampling program. However, during the 1997 Phase I RI field work, a single unplanned groundwater sample (SW7-2GR) was collected from the Grand River. During the Phase I field work, groundwater monitoring well SW7-2 was not installed at the planned location within the boundaries of the former Painesville Township landfill as identified in the RI Workplan. Instead, Ohio EPA requested that the PRP Group install the monitoring well at the west edge of the property, near the bank of the Grand River, in an attempt to move the well outside the clay cover of the landfill. Because the well was installed near the bank of the Grand River, Ohio EPA required the PRP Group to collect a Grand River surface water sample at a location adjacent to monitoring well SW7-2 to compare its analytical results with the SW7-2 groundwater sample results. The Grand River surface water sample SW7-2GR was collected at the same time groundwater sample SW7-2 was collected. Surface water sample SW7-2GR was not collected using methods outlined in the Phase I RI Workplan since a surface water sampling program was not outlined at that time. Rather, an extension rod with an attached, dedicated sample collection container was used to collect the surface water sample by reaching from the river bank. Both the groundwater and surface water samples, SW7-2 and SW7-2GR, were filtered in the field prior to laboratory analysis of metals. SW7-2GR surface water was analyzed for the full suite of analytes to provide a direct comparison to groundwater sample SW7-2.

  Surface water sampling from SW7-2GR and analysis of the samples were not conducted under the approved Phase I RI Workplan. Thus, sampling and analysis of SW7-2GR were not conducted in accordance with the data quality objectives specific to the RI for this Site. Surface water sample SW7-2GR was collected prior to the development of an approved surface water sampling program and target analyte list. A Grand River surface water sampling program and target analyte list were developed and approved in 2000 in the Phase II RI Workplan, three years after the collection of SW7-2GR. For these reasons, analytical data from SW7-2GR were not included in the dataset used to calculate potential site-related risks from exposures to the Grand River.

- *Surface water quality data collected in 2000 and 2001 per the approved Phase II work Plan.* These samples were analyzed for Total Cr, Cr(VI), TOC, alkalinity, TDS, hardness, sulfates, Ca, Mg, Na and Cl.

2.7.2 Data Compilation

The data from studies identified in Section 2.8.1 were compiled in a database format. In the database, the following information is compiled for each surface water and sediment sample analytical record: sample location, unique sample identification, date and time of collection, analytical method, SECOR ID number, chemical name, lab result (concentration), unit of measure, qualifier code, detection flag, and adjusted result (*i.e.*, concentration or one-half the sample detection limit for non-detects).

Grand River surface water samples collected from 22 locations, sediment from 18 locations, and biological sampling data from 6 locations adjacent to the site (RM 2.8 to 5.4) were included in this Lake Erie and Grand River Baseline ERA (Figure 2-20 and Table 2-16). A total of four Lake Erie sediment samples collected during the Phase I RI/FS sampling program were also included in the Lake Erie and Grand River Baseline ERA. Sediment, surface water and biological sample locations included in the Lake Erie and Grand River Baseline ERA are presented in Figure 3-1 of the RI report (SECOR, 2002).

For each sample location for surface water and sediment, analytical results are averaged for sample duplicates and for multiple sampling rounds collected from the same location at the same time. Tentatively identified compounds are identified and eliminated from further consideration in the Lake Erie and Grand River Baseline ERA. Sediment and surface water data used in this Lake Erie and Grand River Baseline ERA are presented in Appendices C, and D, respectively.

2.7.3 COI Selection Process

As described in the approved Lake Erie and Grand River Baseline ERA Work Plan (SECOR, 1997), the purpose of identifying COIs is to focus the Lake Erie and Grand River Baseline ERA on those chemicals which may pose an ecological risk. The selection of COIs in this Lake Erie and Grand River Baseline ERA is consistent with U.S. EPA and Ohio EPA risk assessment guidance (U.S. EPA, 1989a; 1996b) and Appendix G of the *Remedial Investigation/Feasibility Study Work Plan for the Diamond Shamrock Painesville Works Site* (SECOR, 1997).

The terminology used in this document in regard to COI selection is as follows. Detected chemicals are screened to remove Tentatively Identified Compounds (TICs) and to eliminate infrequently detected chemicals. The chemicals not screened by these steps are considered Potential Chemicals of Interest (PCOIs). After further screening as described below, the result is the final list of COIs. Chemical concentrations are evaluated separately for each medium. The COI selection process considers the following factors: (1) removal of TICs, (2) comparison of site concentrations and U.S. EPA's Ecological Data Quality Levels (EDQLs), (3) elimination of essential nutrients and non-toxic chemicals, 4) comparison of site inorganic chemical (metal) concentrations to local background concentrations, (5) comparison to OMZA water quality standards (surface water only) and (6) detection frequency.

2.7.3.1 Tentatively Identified Compounds

The Quality Assurance Project Plan (QAPP) included in the RI Workplan (SECOR, 1997) requires the laboratory to analyze samples only for compounds on the target analyte list for each method. However, the presence of additional organic compounds is often apparent in the analytical results for VOCs and SVOCs. These additional compounds appear as "peaks" on the chromatograms for the analysis. The laboratory is required to identify the 30 highest peaks using computerized search methods. When the mass spectra from the library matches the unknown peaks, the compound is tentatively identified. These compounds are called TICs (U.S. EPA, 1989a). When the unknown peaks cannot be tentatively identified by comparison with mass spectra from the library, a label of "unknown" is recorded.

The following is a summary of the TICs identified during sample analysis. The summary includes all data collected as part of the RI including QA/QC samples:

- Total number of Sample IDs (samples): **2,043**
- Total number of records/analyses: **158,540**
- Total number of analyses that returned either a TIC or a label of "unknown": **12,510**

- Number of analyses that produced TICs: **3,403 (2%)**
- Number of analyses that could not be matched with any known spectra and were labeled "unknown": **9,107 (6%)**

The total of 12,510 TICs and "unknowns" were distributed among media as follows:

- Surface water: 66 analyses
- Soil (includes sediment): 10,517 analyses
- Ground water: 957 analyses
- Water/Liquid: 481 analyses
- Solid: 489 analyses

This summary indicates that the total number of TICs was 2% of analyses, with unknown compounds comprising another 6% of analyses. This rate of TICs is not considered to be a significant portion of the data set.

Because the identity and estimated concentrations for these TICs are highly uncertain, TIC information is often not included in an RI report (U.S. EPA, 1989a). U.S. EPA (1989a) risk assessment guidance recommends that TICs not be included in the risk assessment if only a few TICs are present compared to the target analyte list chemicals, and no historical site information indicates that a particular TIC may indeed be present at the Site. TICs were identified in all areas and media sampled during the RI. Therefore, TICs were not included as COIs in the Lake Erie and Grand River Baseline ERA.

2.7.3.2

2.7.3.2 Ecological Data Quality Levels (EDQLs)

The U.S. EPA's EDQLs were developed based on available federal, state, and international criteria, available toxicity data, and information on chemicals that bioaccumulate in the food chain (U.S. EPA, 1997b). The EDQLS were formulated in 1995, accepted by U.S. EPA Region 5 in 1997, and released for general use in 1998. The EDQLs are primarily intended to help focus and prioritize project objectives and data requirements during the planning and implementation of site-specific RFIs (U.S. EPA, 1997b).

The EDQL values are considered acceptable as analytical detection limits for ecological investigations. Thus, only chemicals that are detected at concentrations above their respective EDQLs (if available) are evaluated further, for the purposes of this Lake Erie and Grand River Baseline ERA. If an EDQL is lacking for a specific chemical, the chemical is selected as a COI for further evaluation, unless other factors in the COI selection process provide a basis for eliminating the chemical from further consideration. The use of data quality objectives in the COI selection process is consistent with the approved Lake Erie and Grand River Baseline ERA Work Plan (SECOR, 1997).

The maximum detected concentration of each chemical is compared to the appropriate surface water or sediment EDQL. In general, if the maximum site concentration exceeds the corresponding EDQL, the chemical is selected as a COI. The only exceptions are metals that are detected at concentrations that are below site-specific background levels, or chemicals that are detected infrequently (see below).

The Region V EDQLs were developed using a three-tiered food-chain approach, as detailed in U.S. EPA, 1999 (Ecological Screening Levels for RCRA Appendix IX Hazardous Constituents, Working Draft, U.S. EPA Region V, 1999). Therefore screening out PBTs that meet their respective EDQLs is protective of species at higher trophic levels. Those PBTs detected at the site that do not meet their EDQL (mercury) are modeled through the food chain.

2.7.3.3 Essential Nutrients

Four metals (calcium, magnesium, potassium, and sodium) detected at the site are considered to be naturally occurring, essential elemental nutrients for plants and animals. EDQLs are not available for these essential nutrients. These essential nutrients are not encountered by aquatic ecological receptors and aquatic-feeding terrestrial wildlife at concentrations sufficient to cause toxicity, and are not included as PCOIs in this Lake Erie and Grand River Baseline ERA.

Section 5.9.4 in U.S. EPA's "Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A)" (RAGS, 1989) states: "Chemicals that are (1) essential nutrients, (2) present at low concentrations (i.e., only slightly elevated above naturally occurring levels), and (3) toxic only at very high doses (i.e., much higher than those that could be associated with contact at the site) need not be considered further in the quantitative risk assessment."

Calcium, magnesium, sodium, potassium and iron are essential nutrients in plants. Calcium and magnesium are secondary macronutrients needed by plants in relatively large amounts, although in smaller amounts than the primary macronutrients (N, P and K). Calcium is an important co-enzyme and structural component of cell walls, among many other functions.

Magnesium is a structural component of the chlorophyll molecule among other important functions. Sodium is considered to be a plant micronutrient for some plant species, small or trace amounts of Na being necessary for osmotic regulation by plant cells. Potassium is a primary plant macronutrient and one of the three principal components of plant fertilizers.

Calcium, magnesium, sodium, and potassium are also essential nutrients in animals. Calcium is an integral component of bones and teeth of vertebrates. Calcium ions are involved in the triggering of muscle contraction and in the activation of calmodulin-mediated enzymes. Magnesium ions are involved in the activation of DNA polymerase and in the regulation of ATP hydrolysis. Sodium ions are essential to the function of sodium ion channels in cellular membranes. Sodium channels are involved in the transmission of nerve impulses, muscle contraction, and in the regulation of cAMP-dependent protein kinases for signal transduction in hormonal communication, photoreception and olfaction. Potassium ions participate in many essential biological processes, such as the maintenance of osmotic potential within cells, nerve impulse transmission, enzyme reactions in cellular metabolism, cardiac, skeletal and smooth muscle function, and the maintenance of normal kidney function.

In general terms, all of these metals are plentiful constituents of uncontaminated mineral soils and sediments. Attempts were made to obtain data on background levels of these five metals in Ohio or Midwest soils and sediments. Data on total concentrations of these metals proved difficult to obtain, because they are considered plentiful and nontoxic elements and are rarely analyzed for in soils (Dr. Warren Dick, Ohio Agricultural Research and Development Center, Wooster, OH, personal communication). Limited data on total soil concentration for Ca and Mg were obtained from Dr. Warren Dick at OARDC's STAR lab (phone 330-263-3877). Dr. Dick and his colleagues analyzed ten soil samples for total Ca and Mg and found that the mean for Ca was 0.582% (5,820 ppm) and the mean for Mg was 0.438% (4,380 ppm)(Dr. Warren Dick, personal communication). The maximum detection for Ca in Grand River sediment at the Site was 158,000 ppm, 27 times the soil mean concentration cited above, while Mg was below background. The maximum detection for Ca in Lake Erie sediment at the Site was 69,200 ppm, 12 times the soil mean concentration cited above, and the maximum detection for Mg was 11,200 ppm, 2.5 times the soil mean concentration cited above.

Ranges of background levels of potassium and sodium in Ohio soils or sediments could not be located. It should be noted, however, that the maximum detection of potassium in Grand River sediments exceeded the site-specific background by only a factor of 1.9, and can be considered slightly elevated. The maximum detection of potassium in Lake Erie sediments was below site-specific background.

The mechanism of calcium toxicity to plants is to produce elevated pH, which limits the growth of plant species adapted for life in circumneutral or acidic soils and sediments. However, many plant species thrive in high pH soils, including native species associated with fen wetland habitats (e.g. *Potentilla quinqefolia*) as well as habitat-generalist species such as *Phragmites communis*, which tend to tolerate broad ranges of environmental conditions. Undisturbed fen sediments commonly include layers of marl, or precipitated $CaCO_3$, within which the Ca concentration is expected to be very high. A cursory search of available literature failed to yield a soil or sediment calcium concentration considered toxic to all plant species.

The mechanism of sodium toxicity to plants is to reduce the osmotic gradient between plant cells and the growth medium, thus reducing the ability of plants to draw moisture and nutrients from the medium. This effect of elevated sodium limits the growth of plant species that lack specific adaptations for dealing with low osmotic gradients. However, many plant species do possess mechanisms for excluding, sequestering or shedding high levels of sodium, for example those species that thrive in or near coastal marshes. In addition, habitat-generalist or tolerant plant species can thrive in areas of elevated sodium up to the concentration in seawater (about 1% or 10 ppt). In general, few plants can survive in sediments where the sodium concentration exceeds 14 ppt (equivalent to 35 ppt NaCl), and probably none can survive in excess of 28 ppt (equivalent to 70 ppt NaCl)(Cronk and Fennessey, 2001). In comparison, the maximum detection of sodium in Grand River sediments at the Site was 9.9 ppt (9,900 ppm), and the maximum detection of sodium in Lake Erie sediments was 1.2 ppt (1,230 ppm). Thus, sodium does not appear to be present at concentrations in sediment that could adversely affect plant growth.

A cursory review of plant physiological literature did not yield a mechanism of magnesium or potassium toxicity to plants, or any levels in sediments at which these elements are thought to be toxic to all plants. A cursory review of animal physiological literature did not reveal any references to toxic doses of Ca, Mg, Na or K.

Of the four metals, calcium does not meet the second of the three RAGS criteria (i.e., present at low concentrations). However, if ranges of background levels of calcium from Ohio sediments were available, including those from Ohio fens, it is likely that calcium would appear less elevated in comparison.

2.7.3.4 Background Comparison

Certain concentrations of metals are present naturally in environmental media. Consistent with the approved Lake Erie and Grand River Baseline ERA Work Plan (SECOR, 1997), and according to U.S. EPA (1989a) guidance, if a metal concentration in a particular medium does not exceed background concentrations in media "native to the property," the metal should not be quantitatively evaluated in a risk assessment. Regional background locations are used for comparing concentrations in media collected from the site to naturally occurring background concentration levels to ensure that quantitative estimates of ecological exposures represent incremental exposures above those associated with background media. In this Lake Erie and Grand River Baseline ERA, if (1) the mean exposure point concentration for an inorganic chemical in a site-related media is less than the mean background concentration, and (2) the maximum detected concentration in site-related media is less than a concentration equal to the mean plus two standard deviations for the background data, then the inorganic chemical is eliminated from further consideration as a COI for that medium. Table 2-17 presents the calculated background concentrations for Grand River sediment, and Grand River surface water. The data sets used to calculate background concentrations are described as follows:

Sediment Background: A data set was compiled of background concentrations of inorganic chemicals in Grand River sediments upstream of the site (RM 5.5 – RM 8.5). Grand River sediment data from seven upstream locations (collected by Ohio EPA between 1994 and 1998) were used to derive an inorganic background data set for sediments of the Grand River (Table 2-17). The sediment background data set was provided by Dennis Mishne, Ohio EPA Division of Surface Water, Columbus.

The sediment background data set for metals derived from Grand River sediments upstream of the Painesville Site is compared to both Grand River and Lake Erie sediment analytical results in the COI selection process. Because of the different hydrologic settings for the Grand River and Lake Erie, a comparison of the Grand River sediment background data set was made to a recently published Lake Erie sediment background data set to determine which data set was the more protective. Ten metals in the Grand River background data set were also analysed in Lake Erie sediments by Painter et al. (2001)(Al, As, Cd, Cr, Hg, Zn, Fe, Cu, Pb, and Ni). Painter et al. (2001) published raw analytical data from 69 Lake Erie sediment samples taken in 1997 and 1998. The data was collected as part of a study of trends in sediment quality undertaken jointly by Environment Canada and Ohio EPA. The sediment samples were taken from zero to three cm and were collected from east, west and central Lake Erie. Painter et al. (2001) analysed these sediment samples for the ten metals listed above plus Mn, as well as N and P. Hull prepared summary statistics for the Painter et al. (2001) sediment data set (n=15) from eastern Lake Erie, and calculated background concentrations (mean + two standard deviations) for the ten metals (Table 2-18): For Cr, Hg, Cu, Pb and Ni, the background calculated from the Grand River data set (see Table 2-17) was lower or more protective. For As, Al, Cd, Fe and Zn, the Lake Erie background was slightly lower or more protective; however, the maximum detection in the Lake Erie Painesville Site sediment data set for each of these metals was below the background numbers for both Lake Erie and Grand River sediments. Therefore, the Grand River sediment background data set was used for COI selection for both the Grand River and Lake Erie, as it is, overall, the most protective available.

Grand River Surface Water Background: A data set was compiled of background concentrations of inorganic chemicals in Grand River surface water upstream of the site (RM 5.5 – RM 8.5). Grand River surface water data from 2 upstream locations (collected by Ohio EPA between 1994 and 2000) were used to derive an inorganic background data set for surface waters of the Grand River. The surface water background data set was provided by Dennis Mishne, Ohio EPA Division of Surface Water, Columbus.

2.7.3.5 OMZA Surface Water Quality Standards

Maximum detected chemical concentrations in surface water from the Grand River are compared to chronic surface water quality standards protective of aquatic life “Outside the Mixing Zone Average” (OMZA) (Ohio EPA, 2002).

2.7.3.6 Detection Frequency

As indicated in the Work Plan (SECOR, 1997), a detection frequency of 5% is used to eliminate infrequently detected compounds from further consideration as COIs in the Lake Erie and Grand River Baseline ERA.

2.7.4 Chemicals Selected as COIs

The results of COI selection are displayed separately for Grand River sediment (Table 2-19; Figure 2-23), Grand River surface water (Table 2-15; Figure 2-22) and Lake Erie sediment (Table 2-20; Figure 2-24). Chemicals selected as COIs are summarized in Table 2-21 and are outlined below:

> **Grand River Sediment:** Seven polycyclic aromatic hydrocarbons (PAHs), total PAHs, one other SVOC, four VOCs, one pesticide, 11 metals, and cyanide.
>
> **Grand River Surface Water:** Three metals (total chromium and filtered and unfiltered hexavalent chromium) and TDS.
>
> **Lake Erie Sediment:** 17 PAHs, total PAHs, two other SVOCs, five pesticides, two metals, and cyanide.

Calcium, magnesium and sodium were detected in Grand River surface water in excess of site-specific background concentrations, but are not individually evaluated in this risk assessment. All three of these metals are eliminated as COIs because they are essential nutrients. However, they are known constituents of Solvay process waste and components of total dissolved solids (TDS). Solvay waste typically consists of 55-75% calcium, 6-9% magnesium and 1-4% sodium (Hou, 1942). Neither EDQLs nor water quality criteria are available for these metals. The elevated levels of these metals in Grand River surface waters is assumed to be due to TDS loading from the Solvay waste ponds. Therefore, these metals are assessed collectively as TDS in this risk assessment.

Iron was below background in surface water and has no Ohio EPA OMZA standard, so it was not selected as a COI. The maximum detection for iron (0.915 mg/L) was also compared with a United States nationwide standard for iron (U.S. EPA 1993a) and found to be below this standard (1.0 mg/L).

It should be noted that historical sources of various chemicals were not evaluated as part of COI selection. For example, although several pesticides are identified as COIs, neither pesticide manufacture nor large-scale (agricultural) pesticide application occurred at the Painesville Site. Possible sources of pesticides at the site include limited application for insect control or aerial deposition from off-site locations. However, pesticides that were not screened out according to the screening procedures detailed above are evaluated in the risk assessment.

Total PAHs as a class were analyzed in sediments in Lake Erie, but PAHs were not analyzed for as a class in Grand River sediments. In computing Hazard Quotients (Section 5.3), HQs for each individual PAH were summed to produce an HQ for total PAHs in both Lake Erie and Grand River sediments. Although reported in the summary statistics for Lake Erie sediment COIs (Table 3-2), the Lake Erie analytical value for Total PAHs as a class was not used in the wildlife risk calculations (Section 5.3) since toxicity information is available on a single chemical basis.

2.8 Assessment and Measurement Endpoints

According to the U.S. EPA (1995a), assessment endpoints are explicit statements of the characteristics of the ecological system that are to be protected. Assessment endpoints either are measured directly or are evaluated through indirect measures. Measurement endpoints represent quantifiable ecological characteristics that can be measured, interpreted, and related to the valued ecological components chosen as the assessment endpoints. The assessment and measurement endpoints apply to the entire aquatic ecosystem, and equally to all organisms and populations within it, including threatened and endangered species. The following assessment and measurement endpoints are used to interpret ecological risks within the Lake Erie and Grand River Baseline ERA study areas:

Assessment Endpoint #1: Survival and maintenance of fish and aquatic invertebrate community structure and function.

Measurement Endpoint: Comparison of COI concentrations in surface water with concentrations associated (in field and laboratory studies) with adverse effects to growth, reproduction, or survival of aquatic organisms. In addition, measurement of the attainment of applicable aquatic life uses. Finally, qualitative comparison with fish tissue concentrations of COIs.

Assessment Endpoint #2: Survival and maintenance of benthic invertebrate community structure and function.

Measurement Endpoint: Comparison of COI concentrations in sediment with concentrations associated (in field and laboratory studies) with adverse effects to growth, reproduction, or survival of benthic invertebrates. In addition, measurement of the attainment of applicable aquatic life uses.

Assessment Endpoint #3: Survival and maintenance of aquatic-feeding terrestrial wildlife populations and communities dependent on the Grand River or Lake Erie.

Measurement Endpoint: Comparison of exposure concentrations of COIs in ingested media and food with concentrations associated with adverse effects to growth, reproduction, or survival of laboratory animals (birds and mammals). Qualitative comparison with fish tissue concentrations for COIs.

2.9 Conceptual Site Model

The conceptual site model, modified from those described in the work plan (SECOR, 1997), is presented in Figures 2-7A (Grand River) and Figure 2-7B (Lake Erie). The models display the direct and indirect pathways through which ROIs might be exposed to COIs in surface water, sediment and groundwater. According to the U.S. EPA (1996a), the conceptual site models provides a text description and visual representation of the pathways from chemical sources to potentially exposed receptors. The objectives of the conceptual site models are to: (1) illustrate the important relationships within the Painesville Site area, and (2) specify exposure scenarios to be evaluated in this Lake Erie and Grand River Baseline ERA.

For benthic invertebrates, all relevant exposure pathways are evaluated collectively based on the Invertebrate Community Index (ICI), an empirical metric that quantifies the relative quality of benthic macroinvertebrate communities. For fish and aquatic invertebrates, the risk assessment is limited to surface water exposures, as data are not available to assess exposures to chemicals in sediment and prey. The surface water exposure pathway to fish and aquatic invertebrates is evaluated based on the Index of Biotic Integrity (IBI) and the Modified Index of Well-Being (MIwb), two empirical metrics that quantify the relative quality of fish communities. All of the pathways to the biotic communities in the Grand River are evaluated collectively through an aquatic life use attainment analysis, which takes into consideration the quality of benthic macroinvertebrate and fish communities in relation to regional reference sites. For wildlife ROIs, the risk assessment is limited to surface water and sediment exposure to COIs including ingestion of sediment and surface water, and ingestion of aquatic food including fish. Dermal uptake of COIs by wildlife ROIs is not evaluated, as fur and feathers greatly limit the absorption of chemicals through the skin, and data are not available to assess dermal exposures.

3.0 EXPOSURE CHARACTERIZATION

Exposure characterization is the process of estimating the magnitude, frequency and duration of site-specific exposure concentrations and doses of chemicals to a receptor. For this Lake Erie and Grand River Baseline ERA, ROIs are potentially exposed to COIs in surface water and sediment, and biota through the exposure pathways identified in the conceptual site model. Benthic invertebrates are evaluated in the Grand River and Lake Erie Study Areas, fish and aquatic invertebrates are evaluated only for the Grand River, and aquatic-feeding terrestrial wildlife (birds and mammals) are evaluated for all areas.

The basic unit of exposure for benthic invertebrates, aquatic organisms and fish is the exposure point concentration (EPC), defined as the concentration of a COI in a specific environmental medium at the point of contact for the receptor. The basic unit of exposure for wildlife (birds and mammals) is the average daily dose (ADD), which incorporates EPCs in specific environmental media and other factors, and is defined as the average mass of a COI ingested per kilogram body weight of the receptor per day (mg/kg-day). Exposure concentrations or doses are characterized for benthic invertebrates (Section 3.1), fish and aquatic invertebrates (Section 3.2), and wildlife (Section 3.4).

3.1 Benthic Invertebrates

Most benthic invertebrates are relatively sessile, and the concentration of a chemical in sediment at a particular location is a suitable indicator of long-term exposure of benthic communities. The distributions of exposures for benthic organisms inhabiting the Grand River and Lake Erie are characterized using summary statistics, which are calculated as follows:

1. Chemical concentrations for each location are estimated, including calculation of one-half the sample detection limit for non-detects, as described in Section 2.3.2.

2. The distribution of concentration values is evaluated using the D'Agostino-Pearson K2 test (D'Agostino *et al.*, 1990). This test characterizes skewness (symmetry) and kurtosis (general form of the distribution) and requires a minimum of eight samples (preferably >20) of which more than half should be detected concentrations. Based on test outcomes, data distributions are described as: (1) normally distributed, (2) lognormally distributed, (3) undefined (does not meet conditions of normality or lognormality), or (4) not tested (does not meet conditions for testing). If the data have an undefined distribution or were not tested, the data are assumed to be lognormally distributed.

3. Data are summarized, including calculation of the detection frequency, minimum and maximum detected concentrations, calculation of the arithmetic mean or best estimate of the mean, and 95th UCL. The arithmetic mean is generally representative of the central tendency of the data; however, in situations where a lognormal distribution has a large number of samples and high variability, the arithmetic mean can exceed the calculated 95th UCL concentration from the lognormally distributed data. In these cases, the "best estimate of the mean" (BEM) (Gilbert, 1987) is used in place of the arithmetic mean.

4. An EPC is calculated. An EPC is a chemical concentration in an environmental medium with which a receptor would come into contact. The value for an EPC is dependent upon the statistical characteristics of the source data, for example, the number of data points, the number of detected values relative to the total number of samples, the non-detect values, the distribution of the data, and other factors. Derivation of an exposure-point concentration is initially based on calculation of the mean, standard deviation, and confidence limits for the concentration of a chemical in the medium, using standard statistical methods.

For Grand River sediments, the EPC was calculated as the 95% UCL of the mean. Although VOCs are not ubiquitous in Grand River sediments, these three sample locations are distributed along a 0.46-mile reach of the river. In addition, because all of the samples were taken from either shallow near-shore water or from the river bank itself, aquatic macroinvertebrate populations would probably not be present at these locations. Therefore, using the 95% UCL of the mean is protective as an exposure point concentration for aquatic life at this site. For Lake Erie sediments, of which there were only four samples, the EPC was set to the maximum detected concentration in sediment. Calculation of a 95% UCL for the limited Lake Erie sediment data set would not adequately reflect the potential for exposure of sessile benthic organisms to localized concentrations of COIs that might exceed the 95% UCL.

For benthic invertebrates, exposures are characterized based on dry-weight sediment concentrations for inorganic COIs and for relatively hydrophilic organic COIs. For hydrophobic COIs having log K_{ow} values (logarithm of the octanol: water partitioning coefficient) greater than 2.0, the most important factor controlling chemical bioavailability in sediment is the concentration of organic carbon (Di Toro *et al.*, 1991). Based on a limited number of samples, Grand River sediments had a mean TOC of 1.32% and a range of 0.53%-2.53% (n=7), and Lake Erie sediments had a mean TOC of 0.4% and a range of 0.4 to 0.5(n=4)(Table 2-13). The combined sediment TOC data for the Diamond Shamrock Site (n=11) yields a mean of 1.00% and a range of 0.4% to 2.53%. Because the mean TOC values for the Grand River and Lake Erie are not substantially different, and because of the proximity of the overall Site mean to 1%, it is unnecessary to calculate exposures for each waterbody based on the site-specific TOC data. Therefore, exposures are normalized to a constant TOC concentration of 1% so that they can be compared with the effects benchmarks provided in Section 4.1. Concentrations of COIs in sediment collected from the Grand River and Lake Erie are summarized in Tables 3-1 and 3-2, respectively.

3.2 Fish and Aquatic Invertebrates

The exposure of fish and aquatic invertebrates to COIs in surface water is affected by the mobility of the organisms and of the water. The mobility of fish warrants that average surface water concentrations be used as the most appropriate representation of exposure to COIs. However, differences among COI concentrations for individual sample locations may reflect temporal as well as spatial differences in exposure, due to the mobility of surface water. Therefore, the distribution of surface water concentrations is used to characterize the range of conditions that a fish may encounter. Summary statistics characterizing COI concentrations in surface water are presented in Table 3-3, and the distributions of detected COI concentrations in surface water are further examined as part of risk characterization (Section 5.0).

As shown in Table 2-15, chromium concentrations in Grand River surface water have been measured using three types of analyses: total chromium (unfiltered), hexavalent chromium (unfiltered), and hexavalent chromium (filtered). Hexavalent chromium (unfiltered) is not a COI since it was eliminated based on the OMZA evaluation (Table 2-15). Total chromium in surface water is expected to include both trivalent and hexavalent chromium; these forms of chromium are evaluated separately because hexavalent chromium is generally more toxic than trivalent chromium. Filtered and unfiltered analyses of hexavalent chromium provide an indication of the amount of chromium that is dissolved in surface water (filtered analyses), as opposed to chromium that may be contained on suspended particles (unfiltered analyses). Paired filtered and unfiltered samples were collected from a location adjacent to Study Area 5 and analyzed for hexavalent chromium as part of a multi-year monitoring program. Additional unfiltered samples from other locations in the Grand River Study Area were also analyzed for hexavalent chromium. The similarity of the results for these three analyses suggests that most of the chromium present in Grand River surface water adjacent to the Painesville Site is present as dissolved hexavalent chromium. However, due to the variety of biotic and abiotic factors influencing the complex speciation of chromium in surface waters (see Section 2.3.1), the relative proportion of the different chromium species cannot be established with complete certainty in the context of this Lake Erie and Grand River Baseline ERA.

3.3 Wildlife

The primary route of exposure to aquatic feeding wildlife receptors is ingestion of food, sediment, and surface water (Figure 3-1). The aquatic pathways shown in Figure 3-1 are addressed in this Lake Erie and Grand River Baseline ERA and the terrestrial pathways will be addressed in the OU risk asessments. The exposure characterization for wildlife ROIs incorporates measured concentrations of COIs in sediment and surface water, and predicted concentrations of COIs in benthic invertebrates and fish as appropriate to a specific ROI. These EPCs are coupled with the ingestion rates and body weights of the receptors to estimate the exposures of the wildlife receptors to chemicals at the Painesville Site. Exposure is quantified as an "average daily dose" (ADD; mg COI ingested per kg body weight per day). An ADD is the sum of exposures to COIs through ingestion of food, surface water, and sediment, and is the average dose that an individual receptor might receive if the receptor foraged only at the Site. The following subsections define the relevant exposure-point concentrations and how the ADD is derived.

3.3.1 Exposure-Point Concentrations in Environmental Media

Exposure-point concentrations (EPCs) of COIs in sediment or surface water are estimated as the 95UCL (or maximum detected concentration if there is only a single detected value) from samples collected from the Grand River or Lake Erie shoreline. EPCs for sediment and surface water are provided in Table 3-4 (Grand River) and Table 3-6 (Lake Erie).

3.3.2 Exposure-Point Concentrations in Benthic Invertebrates and Forage Fish

EPCs in benthic invertebrates and forage fish are estimated because there are few measurements of chemical concentrations from whole-body fish and only limited benthic invertebrate data (two soft-body tissue samples from freshwater mussels) from the Site. A common method of estimating concentrations of chemicals in aquatic organisms involves the use of "uptake" or "accumulation" factors such as BSAFs (biota–sediment accumulation factors) or BCFs (bioconcentration factors). BSAFs are used to predict concentrations of chemicals in an aquatic organism based on concentrations measured in sediment, while BCFs are used to predict concentrations of chemicals in aquatic organisms based on concentrations measured in water. BSAFs provide quantitative indicators of the tendency for a chemical to partition into organisms, relative to the concentrations present in sediment, and in general, provide a less variable and more protective approximation of chemical concentrations in organisms than BCFs.

The use of BSAFs is recommended when appropriate site-specific tissue data are not available (U.S. EPA, 1995b, 1997c).

The BSAFs developed for benthic invertebrates and fish are used to estimate chemical concentrations in these organisms, which are potential food for aquatic invertivorous and piscivorous wildlife ROIs. BSAFs are derived for all COIs, with the exception of organic chemicals having log K_{ow} values below 4, because these chemicals are not considered to significantly bioaccumulate in food webs (Connolly and Pederson, 1988; Thomann *et al.*, 1992). The derivation of BSAFs is described for organic and inorganic COIs below (Sections 3.3.2.1 and 3.3.2.2).

An alternative method of estimating COI concentrations in fish involves employing measured concentrations in fillet samples, which have been collected for the assessment of potential risks to human health. While fish-eating birds and mammals consume whole fish rather than fillets, relationships between whole-body and fillet concentrations have been published in the scientific literature for several chemicals. However, at the Painesville Site, fillet data are available for the Grand River but not Lake Erie. Furthermore, most of the inorganic COIs identified in Grand River sediment were not analyzed in the fillet samples collected by Ohio EPA. Therefore, the BSAF method of estimating COI concentrations is preferred for this Lake Erie and Grand River Baseline ERA. However, the available fillet data are evaluated in comparison to the BSAF-estimated COI concentrations in fish in Section 3.3.2.3.

3.3.2.1 BSAFs for Organic COIs

The partitioning of organic chemicals between sediment and aquatic organisms is controlled primarily by the organic carbon content of the sediment, the lipid content of the organism, and chemical-specific factors. Where possible, empirical data from the scientific literature are used to account for chemical-specific factors that influence partitioning between organic carbon in sediment and lipids in aquatic organisms. BSAFs are normalized to organic carbon content and to lipid content, to allow comparisons among different types of sediments and organisms. Specifically, BSAFs are expressed as the ratio of the lipid-normalized concentration in organisms to the organic-carbon-normalized concentration in sediment:

$$BSAF = \frac{C_{organism} / f_{lipid}}{C_{sediment} / f_{oc}} \qquad (3\text{-}1)$$

where:

BSAF	=	Biota–sediment accumulation factor for aquatic biota (kg organic carbon / kg lipid);
$C_{organism}$	=	Concentration of COI in aquatic biota (mg COI / kg organism, dry weight);
f_{lipid}	=	Fraction lipid in aquatic biota (kg lipid / kg organism, dry weight);
$C_{sediment}$	=	Concentration of COI in sediment (mg COI / kg sediment, dry weight); and
f_{oc}	=	Fraction organic carbon in sediment (kg organic carbon / kg sediment, dry weight).

For this Lake Erie and Grand River Baseline ERA, the literature was reviewed to identify studies that measured chemical accumulation from field-collected sediment and reported the organic carbon and lipid concentrations necessary to derive BSAF values. Studies measuring accumulation from "spiked" sediment were not used, as these studies may overestimate chemical bioavailability by failing to allow sufficient time for equilibration between the dissolved and sediment-adsorbed fractions of the chemical (McFarland *et al.*, 1994).

A compilation by Tracey and Hansen (1996) provides BSAFs for PAHs and pesticides:

Polycyclic Aromatic Hydrocarbons (PAHs). Tracey and Hansen (1996) reviewed the literature related to the bioaccumulation of PAHs into benthic invertebrates (Ankley *et al.*, 1990; Ferraro *et al.*, 1990, 1991; NOAA, 1989, 1991; U.S. EPA, 1990) and developed a distribution of BSAFs based on 843 values for six freshwater and saltwater species (*Crassostrea virginica, Lumbriculus variagatus, Macoma nasuta, Mercenaria mercenaria, Mytilus edulis,* and *Rangia cuneata*). The 90^{th} probability percentile BSAF value for all PAHs (1.71 kg organic carbon / kg lipid) is used as the BSAF for all sediment PAHs at the Painesville Site. By comparison, the median BSAF for PAHs is 0.29 kg organic carbon / kg lipid.

Pesticides. Tracey and Hansen (1996) also reviewed the literature related to the bioaccumulation of pesticides into benthic invertebrates and fish (Ankley *et al.*, 1990; Ferraro *et al.*, 1990, 1991; NOAA, 1989, 1991; Tracey *et al.*, 1991; U.S. EPA, 1990) and developed a distribution of BSAFs based on 765 values for 14 freshwater and saltwater species. The 90^{th} probability percentile BSAF value for all pesticides (7.31 kg organic carbon / kg lipid) is used as the BSAF for all sediment pesticides at the Painesville Site. By comparison, the median BSAF for pesticides is 1.8 kg organic carbon / kg lipid.

The only potentially bioaccumulative organic COI identified in sediment which is not classified as a PAH or pesticide is bis(2-ethylhexyl)phthalate. Sufficient information is not available in the literature to identify a BSAF value for this COI. Therefore, a generalized model (Gobas and McCorquodale, 1992) is used to estimate a BSAF value for benthic invertebrates ($BSAF_{bi}$) and forage fish ($BSAF_{fish}$). The generalized model assumes a thermodynamic equilibrium among chemical concentrations, organic carbon in sediment, and lipid in the organism, without regard to chemical-specific factors that may affect bioaccumulation:

$$\frac{C_{organism}}{f_{lipid}} \approx \frac{C_{sediment}}{f_{oc}} \tag{3-2}$$

where:

$C_{organism}$ = Concentration of a chemical in the organism (mg chemical / kg organism, dry weight);

$C_{sediment}$ = Concentration of a chemical in sediment (mg chemical / kg sediment, dry weight);

f_{lipid} = Fraction lipid in the organism (kg lipid / kg organism, dry weight); and

f_{oc} = Fraction organic carbon in sediment (kg organic carbon / kg sediment, dry weight).

Dividing each side of Equation 3-2 by the $C_{sediment}/f_{oc}$ term, Equation 3-2 can be rearranged to match Equation 3-1, and the relationship is thereby equivalent to an organic carbon- and lipid-normalized BSAF value of 1. Organic carbon- and lipid-normalized BSAF is used to predict wet-weight concentrations in benthic invertebrates or fish by applying study-area-specific dry-weight organic carbon concentrations, estimated lipid concentrations, and dry-weight-to-wet-weight conversion factors according to:

$$C_{organism} = BSAF \times \frac{C_{sediment}}{f_{oc}} \times f_{lipid} \times (DW{:}WW) \tag{3-3}$$

where:

$C_{organism}$ = COI concentration predicted in aquatic biota (mg COI / kg benthic invertebrate or fish, wet weight);

BSAF = Organic carbon- and lipid-normalized BSAF (kg organic carbon / kg lipid);

f_{lipid} = Fraction of lipid in an organism (kg lipid per kg benthic invertebrate or fish, dry weight);

f_{oc} = Site-specific fraction of organic carbon in sediment (kg organic carbon/ kg sediment, dry weight); and

(DW:WW) = Dry-weight-to-wet-weight conversion factor (kg organism dry weight per kg organism wet weight).

Estimated dry-weight lipid content is assumed to be 1% for benthic invertebrates (Connell *et al.*, 1988; Markwell *et al.*, 1989; Oliver, 1984, 1987). An average dry-weight lipid concentration of 1.6% is estimated from forage fish data available in U.S. EPA (1997d) for epibenthic and pelagic species, excluding top predators, that are known to occur in the Grand River (Ohio EPA, 1987; 1995; 1997). The DW:WW conversion factor is 0.16 for benthic invertebrates (kg benthic invertebrate dry weight per kg benthic invertebrate wet weight; =84% moisture) and 0.25 for forage fish (kg fish dry weight per kg fish wet weight; =75% moisture), based on data reported in U.S. EPA (1993b).

The average dry-weight concentrations of organic carbon in Grand River and Lake Erie sediment (0.01 kg oc/kg sediment [1%] and 0.004 kg oc/kg sediment [0.4%], respectively) are less than or equal to estimated dry-weight lipid content for benthic invertebrates and forage fish (1% and 1.6%, respectively). Therefore, on a dry-weight basis, concentrations of all organic chemicals in biota are estimated to be equal to or higher than the concentrations in sediment. BSAF values and estimated concentrations of COIs in aquatic biota are presented in Table 3-4 (Grand River) and Table 3-6 (Lake Erie).

3.3.2.2 Inorganic COIs

For inorganic chemicals, normalizing factors are not available to facilitate comparison of BSAFs among sites, as the factors that affect bioavailability are more complex for inorganic chemicals than for organic chemicals (Anderson *et al.*, 1987). For copper, lead, and zinc, recent advances in sediment toxicity assessment techniques provide a method of identifying sediments in which these metals are not bioavailable (Ankley *et al.*, 1996). However, site-specific measurements remain the preferred method of estimating COI concentrations in biota. For this Lake Erie and Grand River Baseline ERA, BSAFs are estimated in the absence of site-specific biological data. For estimation of concentrations of inorganic chemicals in benthic invertebrates and fish, the BSAF is assumed to be equal to one, which indicates bioaccumulation but not biomagnification.

This generic BSAF is used to predict wet-weight concentrations in benthic invertebrates or fish by applying dry-weight-to-wet-weight conversion factors according to:

$$C_{organism} = BSAF \times C_{sediment} \times (DW:WW) \quad (3\text{-}4)$$

where:

$C_{organism}$	=	COI concentration predicted in aquatic biota (mg COI / kg benthic invertebrate or fish, wet weight);
$C_{sediment}$	=	Concentration of a chemical in sediment (mg chemical / kg sediment, dry weight);
BSAF	=	Organic carbon- and lipid-normalized BSAF (kg organic carbon / kg lipid); and
(DW:WW)	=	Dry-weight-to-wet-weight conversion factor (kg organism dry weight per kg organism wet weight).

BSAF values and estimated concentrations of COIs in aquatic biota are presented in Table 3-4 (Grand River) and Table 3-6 (Lake Erie). Although the extent of measured concentrations of COIs in whole bivalves collected from the Grand River Study Area is too limited to provide a basis for assessing risks to wildlife in this Lake Erie and Grand River Baseline ERA (two samples), analytical results for these samples can be qualitatively compared to the estimated concentrations in Table 3-4. This comparison appears in Table 3-5. The only COIs detected in the two samples were cadmium, chromium, and lead; the measured wet-weight concentrations are much lower than the concentrations estimated for this Lake Erie and Grand River Baseline ERA based on sediment data (Appendix F). Table 3-5 shows that the predicted concentrations are between 47% (cadmium) and as much as 25 times (chromium) higher than the measured concentrations.

3.3.2.3 Comparison of Whole-Fish EPCs Estimated from Sediment v. Fillet Data

Site-specific measured concentrations of COIs in fish include analyses of five edible fillet samples collected from the Grand River. Sampled species included smallmouth buffalo, channel catfish, smallmouth bass, and largemouth bass. Five COIs (bis(2-ethylhexyl)phthalate, heptachlor epoxide, cadmium, chromium, and mercury) were detected in the fillet samples (Ohio EPA, 1995).

For comparison to the EPCs presented in Table 3-4, whole-fish COI concentrations are estimated from fillet concentrations using relationships between whole-body and muscle (fillet) concentrations that have been published in the scientific literature for organic and inorganic chemicals (Bevelhimer *et al.*, 1997). Bevelhimer *et al.* (1997) compared muscle and whole-body concentrations of two organic chemicals (total chlordane and total PCBs) and eleven inorganic chemicals in black bass (*i.e.*, largemouth bass [*Micropterus salmoides*] and spotted bass [*M. punctulatis*]), and channel catfish (*Ictalurus punctatus*). For each species, contaminant-specific equations were developed to describe the relationship between muscle and whole-body concentrations.

Whole-fish COI concentrations are extrapolated from the mean and maximum detected concentrations of bis(2-ethylhexyl)phthalate, heptachlor epoxide, cadmium, chromium, and mercury in fillet tissue, using methods reported in Bevelhimer *et al.* (1997). Chemical-specific extrapolation methods are not available for bis(2-ethylhexyl)phthalate and heptachlor epoxide; therefore, the range of relationships observed for other organic chemicals (chlordane and PCBs) is used to estimate a range of possible whole-body concentrations corresponding to the measured fillet concentrations (Table 3-7). These concentrations are compared to the 95UCL whole-fish concentrations estimated from sediment (Sections 3.4.2.1 and 3.4.2.2). The fillet-based concentrations are higher than the sediment-based concentrations for bis(2-ethylhexyl)phthalate and heptachlor epoxide, lower than the sediment-based concentrations for cadmium and chromium, and similar to the sediment-based concentration for mercury.

The differences between the whole-fish COI concentrations estimated from fillet and sediment data may reflect uncertainties in both types of estimation methods. A potentially more important source of uncertainty, however, is the extent to which fish migrate in and out of the Grand River Study Area. Fish may bioaccumulate pesticides in Lake Erie, for example, prior to being sampled from the Grand River. The fact that all Lake Erie jurisdictions have fish consumption advisories in effect for offshore waters underscores the potential for "contaminated" fish to enter the Grand River from Lake Erie. This issue was addressed, in part, by Ohio EPA's 1998 fish tissue sampling event, which focused on the collection of three non-migratory fish species.

3.3.3 Average Daily Doses (ADDs) to Wildlife ROIs

The ADDs for wildlife receptors are calculated using the EPCs identified for surface water, sediment, and food, and receptor-specific exposure parameters. The ADD represents the average amount of a COI that an individual member of a receptor population would ingest if the receptor foraged in appropriate study areas of the Painesville Site.

<u>Exposure Parameters.</u> Receptor-specific exposure parameters are presented in Tale 3-7. The derivation of these exposure parameters is detailed in Appendix G. With the exception of the sandpiper, the diets of aquatic-feeding wildlife ROIs are represented as a mixture of fish and benthic invertebrates in varying proportions based on comments provided by Ohio EPA, August

29, 2001 (see Figure 3-1). The spotted sandpiper consumes only benthic invertebrates. An ADD for an individual study area is calculated according to:

$$ADD_{Study\ Area} = \frac{IR_{food} \times C_{food}}{BW} + \left[\frac{IR_{sediment} \times C_{sediment}}{BW} \quad OR \quad \frac{IR_{soil} \times C_{soil}}{BW} \right] + \frac{IR_{water} \times C_{water}}{BW} \qquad (3\text{-}10)$$

where:

$ADD_{Study\ Area}$	=	Average daily dose of a COI to an ROI that forages in a study area (mg COI ingested per kg body weight per day);
IR_{food}	=	Ingestion rate of food (kg food, wet weight / day);
C_{food}	=	Concentration of COI in food (mg COI / kg food, wet weight);
BW	=	Body weight of the ROI (kg);
$IR_{sediment}$	=	Ingestion rate of sediment (kg sediment, wet weight / day);
$C_{sediment}$	=	Concentration of COI in sediment (mg COI / kg sediment, wet weight);
IR_{soil}	=	Ingestion rate of soil (kg soil, wet weight / day);
C_{soil}	=	Concentration of COI in soil (mg COI / kg soil wet weight);
IR_{water}	=	Ingestion rate of water (L water / day); and
C_{water}	=	Concentration of COI in water (mg COI / L).

The ADDs calculated for the Painesville Site Study Areas are presented in Table 3-8 and 3-9 (Grand River), Table 3-10 and 3-11 (Lake Erie shoreline).

Mercury Speciation. The calculation of ADDs for mercury requires special attention, as the toxicity of mercury varies over at least an order of magnitude depending on its chemical form. Briefly, mercury can occur in several valence (binding) states, including the monovalent mercurous ion (Hg^{+}), the divalent mercuric ion (Hg^{2+}), and uncharged elemental mercury (Hg^{0}). The ionic forms can combine with other elements to form inorganic salts of mercury, or they can combine with carbon to create a variety of organically complexed compounds. The conversion of inorganic mercury to the methylmercury ion (CH_3Hg^{+}) is the most important process affecting the ecological toxicity and bioaccumulation of mercury. Although methylmercury comprises only a fraction of the total mercury present in sediment and water, its ease in crossing biological membranes and its affinity for sulfhydryl groups in tissue proteins make methylmercury particularly toxic and bioaccumulative (Beckvar *et al.*, 1996).

For this screening ecological risk assessment, the EPCs for total mercury in Grand River sediment are apportioned between inorganic and organic (methylmercury) forms, based on information from U.S. EPA studies and recommendations. U.S. EPA, in the Mercury Study Report to Congress (1997e), assumes that the proportion of methyl mercury can be as much as 15% in sediments. Therefore, for this Lake Erie and Grand River Baseline ERA, the proportion of methyl mercury in sediment is assumed to be 15%.

Methylmercury content is dependent, in part, on trophic level, with predators and scavengers containing a higher proportion of methylmercury than invertebrates that feed at lower trophic levels. Based on a recent study by Becker and Bigham (1995), the percentage of methylmercury in benthic invertebrates is assumed to be approximately 25%.

The speciation of mercury is considerably less variable in fish than in benthic invertebrates. Most recent studies have shown that 95% to 100% of the mercury in fish is methylmercury, although values closer to 80% have also been reported (Eisler 1987; Evans and Engel, 1994; Kannan *et al.*, 1998; Wiener and Spry, 1996). For this Lake Erie and Grand River Baseline ERA, mercury concentrations in forage fish are assumed to be 100% methylmercury.

Chromium Speciation. Chromium occurs in two valence states (trivalent [Cr^{3+}] and hexavalent [Cr^{6+}]). The speciation of chromium in environmental media is complex: Cr^{3+} may oxidize to Cr^{6+} and Cr^{6+} may be reduced to Cr^{3+}. The oxidation of Cr^{3+} to Cr^{6+} in the environment is not typically observed. The chromium oxidation-reduction reaction is influenced by several factors including pH, the relative quantities and reactivity of manganese oxides, and the presence of organic carbon which acts as a reducing agent (James *et al.*, 1997). The valence states of chromium have very different toxicological properties and fate and transport mechanisms. For a more complete discussion of chromium speciation, see Section 2.3.1.

4.0 EFFECTS CHARACTERIZATION

The effects characterization is a qualitative and quantitative description of the relationship between the concentration or dose of a COI and the nature of possible effects elicited in exposed receptors, populations, and/or ecological communities (U.S. EPA, 1995a). An effects characterization is completed separately for the ROIs. The results of this effects characterization and the exposure characterization (Section 3.0) are combined to characterize the risks to ROIs posed by COIs in study areas of the Painesville Site (Section 5.0).

4.1 Benthic Invertebrates

The benthic invertebrate effects characterization is based on published screening-level benchmarks, where available. The effects assessment for PAHs, other organic chemicals, metals, and cyanide are described in the following subsections.

In addition, the benthic invertebrate biological index (Invertebrate Community Index, or ICI) at the Site provides an indication of the biological integrity and health of the benthic community when compared to the promulgated biocriterion. ICI values from the Grand River portion of the Site varied in narrative evaluation from poor to good in the lower part of the site (RM 3.5 and RM 3.9) and were consistently very good in the upper portion of the site (RM 4.7 and RM 5.5)(Table 2-5). The poor ICI score in 2001 contributed to the overall non-attainment of the aquatic life use designation at RM 3.5 in 2001, while ICI was not a factor in non-attainment at this same location in 2000. The ICI score failed in 1994 at RM 3.2, as well. These data indicate an impact to the benthic community is occurring in the vicinity of RM 3.2 to RM 3.5.

4.1.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Numerical sediment quality guidelines (SQGs) have been developed by numerous state, federal, and provincial agencies throughout North America for assessing sediment quality in freshwater and marine ecosystems. These SQGs when used in conjunction with exposure characterization can be used to assess the risks to ROIs posed by COIs in study areas of the Painesville Site.

Various approaches have been used to develop SQGs based on factors such as the receptors that are being considered, the degree of protection afforded, the geographic area and intended uses. Often the difference between the SQGs for a particular chemical of concern can differ by several orders of magnitude. In an effort to find agreement between the various published SQGs, MacDonald *et al.* (2000) developed a consensus based approach for 28 chemicals of concern, including metals, PAHs, hydrocarbons, PCBs, and pesticides.

The first step in developing the consensus based SQGs was to analyze the previously published SQGs to determine their applicability. SQGs were used if the methods used to derive the SQGs were readily apparent, if they were based on empirical data relating contaminant concentration to harmful effects on sediment dwelling organisms, and the SQGs were developed on a *de novo* basis.

From the published SQGs, a threshold effect concentration (TEC) and probable effect concentration (PEC) were derived. The TEC identifies concentrations below which harmful effects on sediment dwelling organisms are not expected. These values were developed by determining the geometric mean of the threshold effect levels, effect range low values, lowest effect levels, minimal effect thresholds and sediment quality advisory levels from the published SQGs. The PEC identifies concentrations above which harmful effects on sediment dwelling organisms frequently occur. These values were developed by determining the geometric mean of the probable effect levels, effect range median values, severe effect levels and toxic effect thresholds from the published SQGs. TEC and PEC values were only calculated for those chemicals of concern that had three or more published SQGs. The range of concentration between the TEC and PEC is neither predicted to be toxic nor nontoxic, and the consensus-based SQGs do not provide guidance in this range.

These consensus-based SQGs were evaluated to determine their ability to correctly classify field-collected sediments as toxic or not toxic, based on measured concentrations of chemical contaminants. This was done by compiling a broad range of sediment toxicity and contamination data from numerous locations throughout the United States. In each sediment sample the concentration of each substance was compared to the consensus-based SQG for that substance. The sediment was considered not toxic if the measured concentration was below the TEC and toxic if above the PEC for that substance. This comparison was done for each of the 28 substances for which consensus-based SQGs were developed. The final step in this evaluation was to determine if the sediment sample was actually toxic to organisms based on various toxicity tests. These tests included survival and growth tests on benthic organisms including amphipods (*Hyalella azteca*), mayflies (*Hexagenia limbata*), midges (*Chironomus* *tentans* or *Chironomus riparius*), a daphnid (*Ceriodaphnia dubia*) and a bacterium (*Photobacterium phophoreum*).

The individual TEC and PECs were considered to be accurate if, based on the above evaluation, they correctly predicted the toxic nature of 75% of the sediment samples. Overall, the TECs for 21 substances, and the PECs for 16 substances were found to accurately predict the absence of toxicity in freshwater sediment samples. Specifically, the predictive ability of TECs for metals ranged from 72% to 82%, for PAHs 71% to 83%, for pesticides 71% to 85%, and PCBs 89%. The predictive ability of PECs for metals ranged from 77% to 94%, for PAHs 92% to 100%, pesticides 73% to 97%, and PCBs was 82%. An additional finding of these studies was that the consensus based SQGs accurately predicted sediment toxicity in samples that contained a mixture of contaminants.

Ingersol *et al.* (2000) performed an additional study to test the ability of the consensus-based SQGs to predict the toxicity of sediments. Their tests included a database of 92 published reports and 1,657 samples from throughout North America (with particular emphasis on the Great Lakes region). The results from this study strongly support the findings from MacDonald *et al.* (2000), that the consensus-based SQGs can be used to reliably predict toxicity of sediment on both a regional and national basis.

The consensus-based TECs and SECs for PAHs are summarized in Table 4-1. Additional SQGs for organic COIs are found in Table 4-2,and additional SQGs for metals are found in Table 4-3.

4.1.2 Other Organic Chemicals

SQGs (MacDonald *et al.,* 2000) are available for additional organic COIs including 4,4'-DDE, 4,4'-DDT, dieldrin, and heptachlor epoxide (Table 4-2).

Where possible, other organic chemicals are assessed using the equilibrium partitioning approach (Di Toro *et al.*, 1991), as follows:

$$SQB = f_{oc} \times K_{oc} \times WQB \tag{4-1}$$

where:

SQB = Sediment quality benchmark;
f_{oc} = Fraction of the total mass of dry sediment that consists of organic carbon, set at 0.01 to provide SQBs that are normalized to 1% TOC;
K_{oc} = Chemical-specific partition coefficient (ratio between amount of chemical adsorbed to organic carbon and amount dissolved in porewater at equilibrium); and
WQB = Water quality benchmark, in this case the porewater LC50.

U.S. EPA has endorsed the use of the equilibrium partitioning approach to derive screening benchmarks for organic chemicals having log K_{ow} values between 2.0 and 5.5 (U.S. EPA, 1996b). On this basis, screening benchmarks are developed for benzene, carbazole, chlorobenzene, ethylbenzene, dieldrin, endosulfan I, and methoxychlor (Table 4-2).

A sediment quality benchmark is not derived for bis(2-ethylhexyl)phthalate (DEHP), because the log K_{ow} exceeds 5.5. Call et al. (2001) evaluated the acute toxicity of DEHP in *Chironomus tentans* via water and sediment exposure. They found that water-only exposure to DEHP was nontoxic to *C. tentans*. Sediment exposure of *C. tentans* to DEHP at a mean concentration of 3,070 mg/kg dry weight of sediment resulted in no reduction in the dry weight of the test organisms over the 10-day test period. Studies of longer-term chronic effects of DEHP on freshwater benthos could not be found. A PEL of 2.7 mg/kg was developed for DEHP in sediments in Florida coastal waters, suggesting that this chemical is toxic to benthos under certain circumstances. This benchmark was derived for marine sediments and considered reliable in that application. However, the applicability of this benchmark to freshwater sediments is uncertain. There is evidence that DEHP biodegrades in environmental media. Cartwright et al. (2000) found that the half-life of DEHP in aqueous solution is <15 days, although Call et al. (2001) found that DEHP in saturated sediment did not decrease over a ten-day period. Staples et al. (1997) found that all eighteen phthalate esthers they tested, including DEHP, had a half-life of 28 days or less in aerobic sewage sludge, but that biodegradation may be slower in anaerobic, cold or oligotrophic environments. These studies suggest that DEHP is relatively nontoxic to benthic invertebrates, and that it biodegrades fairly quickly in the environment. Bis(2-ethylhexyl)phthalate is evaluated with respect to wildlife.

The log K_{ow} value for vinyl chloride is 1.50 (Karickhoff and Long, 1995); therefore, a sediment quality benchmark for vinyl chloride cannot be developed using the equilibrium partitioning approach (U.S. EPA, 1996b). Sediment toxicity data for vinyl chloride are lacking; therefore, in order to evaluate vinyl chloride in sediment, measured concentrations are assumed to be present entirely in porewater. Estimated porewater concentrations (based on assumed sediment moisture content of 50%) are compared to acute and chronic water quality benchmark values. Ohio Numerical Water Quality Criteria or Ambient Water Quality Criteria are lacking for vinyl chloride, but the human health criterion of 5.25 mg/L is based on assessment of vinyl chloride as a human carcinogen and is expected to be lower than an ecological effects threshold.

Sediment quality benchmarks cannot be developed using the equilibrium partitioning approach for 4,4'-DDE, 4,4'-DDT (log K_{ow} values exceed 5.5) or heptachlor epoxide (no water quality benchmark is available). However, SQGs (MacDonald et al., 2000) are available for these COIs.

4.1.3 Metals

The benthic invertebrate effects assessment for metals in this Lake Erie and Grand River Baseline ERA uses a weight-of-evidence interpretation of association-based benchmarks that do not necessarily reflect cause-effect toxicological relationships. The only available assessment methods for metals in sediment are based on cause-effect data from controlled experiments that require specialized data collection methods (Ankley *et al.*, 1996). The sediment quality benchmarks used to assess metals in this Lake Erie and Grand River Baseline ERA are described below:

> **Effects Range-Low (ER-L) Benchmark:** The National Oceanic and Atmospheric Administration (NOAA) collects and chemically analyzes sediment from freshwater, estuarine, and marine environments as part of the National Status and Trends (NS&T) Program. ER-L values have been derived from NS&T results and other data to provide a method of ranking chemical concentrations in sediment. The ER-Ls from Long and Morgan (1991) were derived from a data set with a large freshwater component and are selected for use in this report instead of the more recent ER-Ls (Long *et al.*, 1995) derived exclusively from estuarine and marine data.
>
> The data set used to derive ER-Ls primarily includes results of various methods for evaluating synoptically collected biological and chemical data from field surveys. A small number of concentrations derived from the equilibrium partitioning approach (see above) and spiked sediment toxicity testing are also included. The chemical concentrations

observed or predicted by the different methods to be associated with biological effects were sorted, and the 10th-percentile concentrations were identified. The ER-L represents a concentration below which adverse biological effects are not anticipated.

The predictive ability of the ER-L approach to deriving sediment quality benchmarks has been evaluated for the marine benchmarks developed by Long *et al.* (1995). O'Connor *et al.* (1998) found that sediment samples are rarely toxic if all chemical concentrations are below ER-L values.

Lowest Effects Level (LEL) Benchmark: The OME derived LELs as part of the In-Place Pollutants program (Jaagumagi, 1993a, 1993b, 1994; Persaud *et al.*,1993). The OME sampled a total of 326 stations from 20 different areas of concern on the Great Lakes. Sediment assessments included: (1) chemical analysis of the sediments, (2) chemical analysis of benthic invertebrate organisms, and (3) analysis of bottom feeding organisms.

OME's LEL were developed using benthic community data, and are based on the assumption that the distribution of benthic organisms was primarily related to the levels of chemicals measured in the sediment. No toxicity test results were considered, and the approach did not consider the confounding effects of chemical mixtures or physical habitat impairment. Therefore, LELs may be highly over-conservative in some cases (Barber *et al.*, 1997).

The NOAA and OME benchmarks used in this Lake Erie and Grand River Baseline ERA are summarized in Table 4-3. These benchmarks are interpreted using a weight-of-evidence approach in Section 5.0.

As described in Section 4.1.1, consensus-based SQGs (MacDonald et al., 2000) are available for some metal COIs including arsenic, total chromium, lead, mercury and nickel.

The potential for sediment toxicity cannot be assessed for several COIs due to a lack of toxicological information. These COIs include barium, beryllium, cobalt, cyanide, selenium, thallium, and vanadium. These COIs are evaluated for wildlife ROIs but cannot be evaluated for benthic invertebrates. Uncertainty associated with COIs for which benthic invertebrate effects information is lacking is discussed in Section 5.

4.2 Fish and Aquatic Invertebrates

The effects characterization for fish and aquatic invertebrates includes three COIs: total chromium, hexavalent chromium, and total dissolved solids (TDS). For the Lake Erie and Grand River Baseline ERA, these COIs are assessed based on comparisons of site data with Ohio Numerical Water Quality Standards (Table 4-4). State-mandated water-quality criteria (ONWQC) generally supersede federal Ambient Water Quality Criteria (AWQCs) for all state waterways (U.S. EPA, 1996b). Acute and chronic criteria are used to evaluate direct toxicity from short- and long-term exposures, respectively, although they do not correspond to specific levels or types of adverse effects for any particular organism (Suter *et al.*, 1987; U.S. EPA, 1996b). Adverse effects on exposed aquatic biota may occur if either acute or chronic benchmarks are exceeded. There is little likelihood that exposure concentrations lower than chronic benchmarks pose a hazard to exposed organisms (U.S. EPA, 1996b). Because the ONWQC are established to be protective of aquatic life, they are capable of supporting the parallel goals of the Ohio EPA biocriteria program. That is, the presence of chemicals in surface water below ONWQC is not expected to have adverse impacts on aquatic communities such that they fail to meet applicable biocriteria. This expectation is true for all chemicals for which chemical criteria have been developed, including bioaccumulative chemicals such as mercury. Thus, the use of ONWQC as screening benchmarks is justified at this stage of the risk assessment process when the protection endpoint is aquatic communities as quantitatively described through use attainment analysis.

Two types of ONWQC criteria are evaluated (OAC 3745-1-07). The "chronic aquatic criterion" (CAC) is the maximum concentration of a chemical at which no chronic effects occur to aquatic organisms exposed for periods averaging 30 days. The CAC is equivalent to the OMZA standard. The "acute aquatic criterion" (AAC) is the maximum concentration at which no acute effects occur to aquatic organisms exposed for brief (unspecified) periods. The AAC is equivalent to the OMZM standard. Criteria of these types are intended to protect, with reasonable confidence, most aquatic species most of the time (Suter and Tsao, 1996). Although acute criteria are presented, strategic decisions in the risk assessment process are made using chronic toxicity criteria or appropriately adjusted acute levels.

4.3 Toxicity Reference Values for Wildlife

This section provides information on the potential effects of COIs in the four aquatic-feeding wildlife ROIs. The types of effects evaluated are those considered relevant to the assessment endpoints for the Lake Erie and Grand River Baseline ERA (growth, reproductive, developmental, and survival effects), because these may affect the abundance or reproductive success of the receptor populations. The dose-response relationships for COIs are expressed as toxicity reference values (TRVs) for aquatic-feeding wildlife ROIs, which are defined as a daily ingested amount that is associated with a specified effect in the receptor.

TRVs are derived for all sediment, and surface water COIs, with the exception of total dissolved solids and components associated with TDS originating from Solvay waste lacking toxicity information (i.e., calcium, magnesium, and sodium), parameters that are unlikely to affect aquatic-feeding wildlife. For each COI and each wildlife ROI, TRVs are derived to represent both a no observed adverse effect level (NOAEL) and a lowest observed adverse effect level (LOAEL). The NOAEL corresponds to the greatest exposure associated with no observed adverse effects on growth, reproduction, or survival. The LOAEL corresponds to the smallest exposure associated with observed adverse effects on growth, reproduction or survival. The procedures and assumptions used to develop the TRVs are described in the following subsections.

4.3.1 Data Sources

For this analysis, dose-response data were obtained from several sources:

- Ecological Risk Screening-Benchmarks (Sample *et al.*, 1996);
- The U.S. EPA's Technical Support Document for the Hazardous Waste Identification Rule: Risk Assessments for Human and Ecological Receptors (U.S. EPA, 1995c);
- The U.S. Fish and Wildlife Service's Contaminant Hazard Reviews;
- The U.S. EPA's Ambient Water Quality Criteria;
- The Registry of Toxic Effects for Chemical Substances (NIOSH, 1996);
- The U.S. EPA's Integrated Risk Information System (U.S. EPA, 1996c);
- The U.S. EPA's Health Effects Assessment Summary Tables (U.S. EPA, 1995d);

- The Installation Restoration Program Toxicology Guide (DOE, 1989);
- Toxicological Profiles prepared by the U.S. Department of Health and Human Services' Agency for Toxic Substances and Disease Registry; and
- The World Health Organization's Environmental Health Criteria.

These sources represent readily available summaries of wildlife and laboratory-species toxicity data. If necessary, additional information was obtained through literature searches and retrievals from bibliographic databases (*e.g.*, BIOSIS) and searches of other computerized databases containing toxicological data (*e.g.*, AQUIRE).

4.3.2 TRV Derivation Procedures

A variety of approaches are available for deriving TRVs for specific wildlife species, including regression analyses, toxicity testing, application of extrapolation and uncertainty factors, probabilistic analyses, and others. For this evaluation, extrapolation and uncertainty factors (EFs and UFs) are used to derive NOAEL and LOAEL TRVs for wildlife ROIs from laboratory study results, based on the methodology of Sample *et al.* (1996). This process involves the determination of a "test species dose" for a critical endpoint from a particular experimental combination of exposure concentration, exposure duration, test species, and COI. The test-species dose from the selected study is then modified to account for the various extrapolations and uncertainties inherent in applying results from a controlled setting to an ecologically relevant setting, as in:

$$TRV = \frac{\text{Test-Species Dose} \times \text{Dose-Matrix EF}}{\text{Duration UF} \times \text{Endpoint UF}} \times \text{Body-Weight EF} \qquad (0\text{-}1)$$

Extrapolation and uncertainty factors are based on: (1) the dosing matrix used in a laboratory study, (2) the duration of exposure, (3) the endpoint measured, and (4) differences in body weights among test and receptor species (Calabrese and Baldwin, 1993; Ford *et al.*, 1992; Opresko *et al.*, 1994; Sample *et al.*, 1996; U.S. EPA, 1996d; Watkin and Stelljes, 1993; Wentsel *et al.*, 1994). Table 4-5 presents a summary of the uncertainty and extrapolation factors; their derivation and use is described in the following subsections. The use of surrogate chemical data is also discussed.

4.3.2.1 The Test-Species Dose

Critical toxicological values are identified from carefully qualified primary and secondary literature references. The selection of particular studies and endpoints used for the derivation of

TRVs is based on the evaluation of the applicable studies and the dose-response data contained therein. In cases where preferred toxicological endpoints are not available, other toxicity values are used, but additional uncertainty factors may be incorporated. All toxicological values chosen for TRV derivation are presented on a mg COI per kg body weight per day (mg/kg BW-day) basis. These units allow comparisons among organisms of different body sizes (Sample *et al.*, 1996).

The test species dose is a daily dose of a chemical associated with a particular endpoint and effect. In some cases, this dose is explicitly stated within the study; in other cases, only partial or related information is available. For studies which report an effects level as a concentration in food or drinking water, but do not report specific body weights or feeding rates of the test species, default weights and feeding rates (Table 4-6) are used to derive the test species dose:

$$Dose_t = \frac{\text{Cfood}_t \times IR_{food}}{BW_t} \qquad (0\text{-}2)$$

or:

$$Dose_t = \frac{\text{Cwater}_t \times IR_{water}}{BW_t} \qquad (0\text{-}3)$$

where:

$Dose_t$ = Test species dose of a COI (mg COI / kg BW-day);
$Cfood_t$ = Concentration of COI in food (mg COI / kg food);
IR_{food} = Ingestion rate of food by the test species (kg / day);
BW_t = Body weight of the test species (kg);
$Cwater_t$ = Concentration of COI in water (mg COI / L); and
IR_{water} = Ingestion rate of water by the test species (L / day).

4.3.2.2 Dose-Matrix Extrapolation Factors

Exposure estimates are based on ingestion of chemicals, primarily as components of solid matrices like food, soil, or sediment. Because the administration of a chemical in a controlled study may have used a liquid dosing matrix (*e.g.*, water or corn oil), a review of the toxicological data was made to assess differential effects due to the dosing matrix. If a "dose matrix effect" is indicated, an extrapolation factor is incorporated to account for the differential effects of the dosing matrix.

No comprehensive summaries of dose matrix extrapolation factors were identified. Data for only one chemical, lead, indicated that use of a dose-matrix factor would be appropriate. An extrapolation factor of 3 is established to estimate equivalent food doses from toxicity studies in which the test organism was dosed via a drinking water matrix, based on two studies

(Hilderbrand *et al.*, 1973 and Chowdhury *et al.*, 1984). Both studies evaluated laboratory rats for testicular atrophy following subchronic exposure to lead acetate. Hilderbrand *et al.* (1973) reported a LOAEL of 286 mg/kg BW-day in rats dosed orally in the diet, while Chowdhury *et al.* (1984) reported a LOAEL of 100 mg/kg BW-day for rats dosed via drinking water.

The extrapolation factor is a ratio estimating the relative difference between the dose via drinking water versus a dietary dose. A ratio of 3 is calculated by dividing the dietary dose of 286 mg/kg BW-day by the drinking water dose of 100 mg/kg BW-day. This factor represents the multiple of a lead concentration that a test organism must receive via food to produce an equivalent effect to that produced via a drinking water dose.

4.3.2.3 Duration Uncertainty Factors

Exposure durations of interest include (1) chronic, (2) subchronic, and (3) acute. Chronic studies occur over the lifetime or a majority of the lifespan of the test organism, generally longer than one year for mammals and 10 weeks for birds. Additionally, studies in which the test organism is dosed during a critical life stage (*e.g.*, gestation) are included with chronic duration studies. Subchronic studies include exposures of two weeks to one year in duration that do not occur during a critical life stage. Acute studies typically have exposures of less than two weeks. $NOAEL_t$s and $LOAEL_t$s are usually reported from chronic and subchronic studies, with acute studies often reporting frank effect levels (FEL_ts; doses corresponding to the overt expression of a serious adverse effect such as mortality). Test-species doses from chronic studies are used preferentially over data from acute and subchronic studies. In cases where chronic data are not available as test-species doses, studies involving less-than-chronic exposures are used to in the TRV derivation with the addition of a duration uncertainty factor.

A number of factors are suggested to account for differences in exposure duration, but these factors are generally not well documented. An evaluation of available data on the ratios of acute and subchronic $NOAEL_t$s to chronic $NOAEL_t$s (McNamara, 1976; U.S. EPA, 1996d; Weil and McCollister, 1963) indicates that approximately 90% of the acute-to-chronic or subchronic-to-chronic ratios are less than 8, and the 50^{th}-percentile ratio is approximately 3. Based on these data, an uncertainty factor of 3 is applied to a subchronic test-species $dose_t$, and a factor of 8 to an acute test-species dose.

4.3.2.4 Endpoint Uncertainty Factors

Additional uncertainty factors are used to account for uncertainties in extrapolation between effect- and no-effect levels. Specifically, a $NOAEL_t$ test-species dose may be estimated from a $LOAEL_t$ (or FEL_t) value, or a $LOAEL_t$ may be estimated from a FEL_t.

Extrapolation from a $LOAEL_t$ or FEL_t to a $NOAEL_t$: An uncertainty factor of 10 is often used with $LOAEL_t$ values to estimate the $NOAEL_t$ (Opresko *et al.*, 1994; Sample *et al.*, 1996) and is considered protective (Sample *et al.*, 1996; U.S. EPA, 1996d). Uncertainty factors less than 10 may be used if specific information is available which characterizes the dose-response relationship for the observed adverse effect (U.S. EPA, 1996d). When a $LOAEL_t$ value is not available, a FEL_t is used, although chronic $NOAEL_t$s may range from 1/10 to 1/10,000 of the corresponding acute FEL_t value (Opresko *et al.*, 1994). An uncertainty factor of 50 is used to estimate a $NOAEL_t$ value from a FEL_t value for this Lake Erie and Grand River Baseline ERA.

Extrapolation from a FEL_t to a $LOAEL_t$: An uncertainty factor of 50 is used to estimate a $NOAEL_t$ value from a FEL_t value, and an uncertainty factor of 10 is often used to extrapolate from a $LOAEL_t$ to a $NOAEL_t$. Therefore, it is implied that a UF of 5 should be used to extrapolate from an acute FEL_t to an acute $LOAEL_t$.

4.3.2.5 Body-Weight Extrapolation Factor

This extrapolation is accomplished using a body weight-scaling factor to account for differences in body size (Sample *et al.*, 1996). Numerous studies have shown that many physiological functions such as metabolic rates and responses to chemicals are a function of body size for mammals. Smaller mammals have higher metabolic rates and are usually more resistant to chemicals because of more rapid rates of detoxification. It has been shown that the best measure of body size is one based on body surface-area, which can be expressed in terms of body weight raised to a fractional power (Opresko *et al.*, 1994; Sample *et al.*, 1996; U.S. EPA, 1980). Dosimetric differences between the mammalian test species and wildlife receptors are accounted for using:

$$NOAEL_w = NOAEL_t \times \left(\frac{BW_t}{BW_w} \right)^{0.25} \quad (0\text{-}4)$$

where:

$NOAEL_w$ = NOAEL for the mammalian wildlife ROI (mg/kg BW-day);
$NOAEL_t$ = NOAEL for the mammalian test species (mg/kg BW-day);
BW_t = Test species body weight (kg); and
BW_w = Wildlife ROI body weight (kg).

Mammalian wildlife ROI body weights, laboratory test species body weights, and body-weight extrapolation factors are presented in Table 4-7.

Scaling factors may not be appropriate for avian interspecies extrapolations. Recent information has shown that adjustment factors based on body size for interspecies extrapolation among avian species range from 0.63 to 1.55 (Sample *et al.*, 1996). Therefore, a body-weight extrapolation factor is not used to derive avian TRVs.

4.3.2.6 Use of Chemical Surrogates

Toxicity information is not available for all COIs. However, in limited cases, chemical information is available for compounds with generally similar chemical structures or properties that can be used to provide surrogate toxicity information for chemicals that lack specific toxicity information. The estimation of the potential for adverse effects through the use of the chemical surrogate is a better choice than under-characterization of the potential for adverse effects associated with the lack of a TRV.

Quantitative toxicological information is unavailable for many of the individual polycyclic aromatic hydrocarbon (PAH) compounds and for several pesticides. For these compounds, toxicity information from chemical surrogates is utilized as described below:

- A toxicity value for benzo(a)pyrene (Mackenzie and Angevine, 1981) is used as a surrogate value for mammalian exposure to benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and phenanthrene. Although carcinogenicity varies among these compounds, they have generally similar structures and metabolism and are expected to show similar non-carcinogenic toxicity.

- A toxicity value utilizing a PAH mixture (Patton and Dieter, 1980) is used as a surrogate value for birds exposed to acenaphthylene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, indeno(1,2,3-cd)pyrene, 2-methylnaphthalene, naphthalene, and pyrene.

- A toxicity value for naphthalene (NTP, 1991) is used as a surrogate value for mammals exposed to 2-methylnaphthalene. Based on structural similarity and a general similarity in metabolism (ATSDR, 1993a), significant differences in toxicity between these two compounds are not expected.

- Toxicity values for endosulfan were used as surrogate values for mammals and birds exposed to endosulfan I. Technical-grade endosulfan contains at least 94% endosulfan I and endosulfan II.

- Toxicity values for endrin were used as surrogate values for mammals and birds exposed to endrin aldehyde. Endrin aldehyde is produced by the transformation or degradation of endrin following ultraviolet irradiation from sunlight (ATSDR, 1994).

4.3.2.7 Protection of Rare, Threatened and Endangered Species (RTE)

A TRV derived for any PBT compound is protective of an RTE population if it was derived by one or more of three methods:

1. The TRV was derived on the basis of chronic, subchronic or acute adverse effects to individual organisms in a population;

2. The TRV was derived using a food chain multiplier representative of an appropriate trophic level for the RTE population of interest; or

3. The TRV was derived on the basis of a toxicity test using the RTE species of interest as a test organism, or by the application of one or more uncertainty factors, including an allometric scaling factor or an uncertainty factor which otherwise accounts for interspecies differences; or an uncertainty factor specifically protective of an RTE species, or otherwise protective of a sensitive subpopulation (i.e., intraspecies differences in sensitivity).

The TRVs presented in this risk assessment were derived on the basis of chronic, subchronic or acute adverse effects to individual organisms in a population. A considerable margin of safety is incorporated in each TRV by the following: (1) the application of a body-weight extrapolation factor, when both the test species and the receptor population of interest are mammals; the body-weight extrapolation factor corrects for the presumptive detoxification resulting from the more rapid metabolism associated with smaller body weight; (2) the application of an uncertainty factor to account for duration of the toxicity study, including an uncertainty factor of 3 to convert a value from a subchronic study to a chronic value; and an uncertainty factor of 8 to convert a value from an acute study to a chronic value; and (3) the application of an uncertainty factor to account for differences in the measured toxicity endpoint, including an uncertainty factor of 5 to convert an FEL to a LOAEL; an uncertainty factor of 10 to convert a LOAEL to a NOAEL; and an uncertainty factor of 50 to convert a FEL to a NOAEL. Thus, each TRV is protective of individual RTE organisms in a population, as each TRV is based upon adverse effects to an individual organism in a population, and is not based on population effects. Additionally, the TRVs account for interspecies differences by means of an allometric scaling factor amongst mammal species.

4.3.3 Summary of TRVs

TRVs are summarized in Tables 4-8 (bird NOAEL TRVs), 4-9 (bird LOAEL TRVs), 4-10 (mammal NOAEL TRVs), and 4-11 (mammal LOAEL TRVs).

5.0 RISK CHARACTERIZATION

The final step in the Lake Erie and Grand River Baseline ERA, risk characterization, involves the integration of the results of the exposure and effects assessments (Sections 3 and 4) to describe the nature and likelihood of adverse effects associated with exposure to COIs at the Painesville Site. Subsequent sections present risk estimation, discuss associated uncertainties, and interpret the findings for benthic invertebrates (Section 5.1), fish and aquatic invertebrates (Section 5.2), and wildlife (Section 5.4).

5.1 Benthic Invertebrates (Sediment)

The risk characterization for benthic invertebrates in the Grand River and the Lake Erie shoreline is based on the comparison of measured concentrations of COIs in sediments (Tables 3-1 and 3-2; Appendix C) with the sediment quality benchmarks described in Section 4.1 (Tables 4-1 through 4-3). As discussed in detail in Section 4.1, bis(2-ethylhexyl)phthalate in sediment is essentially non-toxic to benthic invertebrates and biodegrades relatively quickly, and is not evaluated further in this section.

In addition, the benthic invertebrate biological index (Invertebrate Community Index, or ICI) at the Site provides an indication of the biological integrity and health of the benthic community when compared to the promulgated biocriterion. It should be noted, however, that biocriteria assessments do not consider the potential for bioaccumulation. ICI values from the Grand River portion of the Site varied in narrative evaluation from poor to good in the lower part of the site (RM 3.5 and RM 3.9) and were consistently very good in the upper portion of the site (RM 4.7 and RM 5.5)(Table 2-5). The poor ICI score at RM 3.5 in 2001 contributed to the overall non-attainment of the aquatic life use designation that year, while ICI was not a factor in non-attainment at this same location in 2000. The ICI score failed to meet its biocriterion in 1994 at RM 3.2 as well. These data indicate an impact to the benthic community is occurring in the vicinity of RM 3.2 to RM 3.5. As discussed in detail in Section 2.1.3.6, the observed impact could potentially be attributed to a number of possible causes including pollutant stressors, lacustuary effects, and habitat quality and changes.

5.1.1 Risk Estimation

5.1.1.1 Grand River

The risk characterization for benthic invertebrates is discussed below for PAHs, other organic chemicals, and inorganic chemicals identified as COIs in Grand River sediments.

PAHs

PAHs in Grand River sediment are assessed using the consensus-based sediment quality guidelines (SQGs) developed by MacDonald et al. (2000) and tested by Ingersoll et al. (2000), as shown in Table 5-1. At least one PAH was detected in a total of six sediment samples collected from the Grand River Study Area. Five PAHs (chrysene, fluoranthene, phenanthrene, pyrene, and benzo(a)anthracene) and Total PAHs were detected at concentrations above the Threshhold Effects Concentration (TEC), but below the Probable Effects Concentration (PEC), indicating that toxicity to benthic invertebrates is indeterminate. One PAH (naphthalene) was detected at a concentration above the PEC at three locations, indicating that toxicity to benthic invertebrates from naphthalene is probable. The locations where PAHs were detected in Grand River sediments are adjacent to Study Areas 4, 5 and 6. These Study Areas are not currently or historically the location of activities generating PAHs, and thus are not considered potential sources of these compounds.

Other Organic Chemicals

Other organic chemicals identified as COIs in Grand River sediment include benzene, chlorobenzene, ethylbenzene, heptachlor epoxide, and vinyl chloride. As described in Section 4.1, these chemicals are assessed (1) using the equilibrium partitioning approach (benzene, chlorobenzene, and ethylbenzene), (2) through comparison with other published benchmarks (heptachlor epoxide), or (3) through a direct comparison to water quality benchmarks (vinyl chloride). Based on the appropriate benchmark comparisons (Table 5-2), ecological effects are unlikely from exposures of benthic invertebrates to benzene, chlorobenzene, ethylbenzene, heptachlor epoxide and vinyl chloride in Grand River sediment.

Inorganic Chemicals

The potential for effects of metals on benthic invertebrates is assessed primarily based on four sets of published benchmarks described in Section 4.1.3 (Table 4-3), which are interpreted using a weight-of-evidence approach. These benchmarks include the ER-L developed by NOAA (Long and Morgan, 1991);OME's LEL values (Jaagumagi, 1993a; Persaud *et al.*,1993); and consensus-based TEC and PEC Sediment Quality Guidelines (SQGs) (MacDonald et al., 2000). If the arithmetic mean concentration for an inorganic chemical detected in sediment is less than the ER-L and LEL, toxicity to benthic invertebrates due to exposure for that particular inorganic chemical is considered to be unlikely. If the 95% UCL for an inorganic chemical detected in sediment is less than the TEC, toxicity to benthic invertebrates is unlikely; if the 95% UCL is greater than the PEC, toxicity to benthic invertebrates is probable. These comparisons appear in Table 5-3.

The following inorganic chemicals are identified as COIs in Grand River sediment: antimony, arsenic, barium, beryllium, chromium (total and hexavalent), cyanide, lead, mercury, nickel, selenium, and vanadium. Based on the comparisons described above, ecological effects are unlikely from exposures of benthic invertebrates to lead and nickel. The potential for sediment toxicity to benthic invertebrates cannot be assessed for barium, beryllium, cyanide, hexavalent chromium, selenium, and vanadium. Uncertainty associated with COIs for which benthic invertebrate effects information is lacking is discussed in Section 5.1.2. The remaining COIs (antimony, arsenic, total chromium, and mercury) are discussed below.

Antimony: Antimony was detected in only one of eight analyses of Grand River sediment at a concentration of 4 mg/kg, which is similar to the ER-L of 2 mg/kg. O'Connor *et al.* (1998) have shown that ER-L/ER-M benchmarks are often overly protective as predictors of sediment toxicity (see Section 4.1). Thus, the presence of antimony in only a single sediment sample at a concentration slightly higher than the ER-L does not indicate a significant potential for adverse effects on benthic invertebrates.

Arsenic: The arithmetic mean concentration of arsenic in Grand River sediment (11.8 mg/kg) exceeds the LEL (6 mg/kg), but not the ER-L (33 mg/kg). Similarly, the 95% UCL of the mean arsenic concentration (15.7 mg/kg) exceeds the TEC (9.79 mg/kg), but not the PEC (33 mg/kg). The site-specific mean background level of arsenic in sediment is 8.3 mg/kg (mean+2SD = 14.9 mg/kg; Table 2-18). Because the arithmetic mean concentration of arsenic detected in sediments is only slightly elevated above background, and because the 95% UCL of the mean arsenic concentration is below the PEC, adverse effects on benthic invertebrates due to arsenic in Grand River sediment are considered unlikely.

Total Chromium: Total chromium was detected in seventeen of eighteen samples collected from sediment in the Grand River. The arithmetic mean concentration for total chromium (25.8 mg/kg) is less than both the ER-L and LEL. The 95% UCL of the mean total chromium concentration exceeds the TEC, but is below the PEC value. Given the low average total chromium concentration, adverse effects on benthic invertebrates due to total chromium in Grand River sediment are considered unlikely.

Mercury: Mercury was detected in two of ten sediment samples at concentrations of 0.26 and 0.71 mg/kg, which are slightly above the ER-L/LEL. The 95% UCL of the mean mercury concentration is between the TEC and PEC. As discussed in Section 3.3.3, 15% of total mercury in sediment is assumed to be present in the methylmercury form. The studies on which MacDonald et al. (2000) based the development of the TEC and PEC values for mercury were empirical studies of chronic effects on benthic organisms, and the organisms in these studies were presumably exposed to some level of methylmercury in sediment. Given the presence of mercury in a small number of sediment samples at concentrations below the PEC, adverse effects on benthic invertebrates are considered unlikely.

In summary, chrysene, fluoranthene, phenanthrene, pyrene, and benzo(a)anthracene in Grand River sediments pose an indeterminate risk to benthic invertebrates while risk from naphthalene is probable.

5.1.1.2 Lake Erie

The risk estimation for benthic invertebrates is discussed below for PAHs, other organic chemicals, and inorganic chemicals detected in Lake Erie sediments. The approaches used to assess these groups of chemicals in sediment are discussed above for the Grand River (Section 5.1.1.1).

PAHs

PAH detections and consensus-based SQGs for PAHs (MacDonald et al., 2000) in Lake Erie sediment samples are shown in Table 5-4. Ten PAHs (naphthalene, fluourene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene) and Total PAHs were detected at concentrations above the TEC at at least three of the four sample locations, and the same ten PAHs and Total PAHs were found above the PEC in at least one location. The potential for toxicity of acenaphthylene, acenaphthene, and benzo(b)fluoranthene to benthic invertebrates could not be determined, because no SQGs have been published for these compounds. These results indicate that toxicity to benthic invertebrates due to the ten individual PAHs and Total PAHs in Lake Erie is probable.

Other Organic Chemicals

Other organic chemicals evaluated in Lake Erie sediment include carbazole and pesticides (4,4'-DDE, 4,4'-DDT, dieldrin, endosulfan I, and methoxychlor). Endosulfan 1 and methoxychlor are assessed using the equilibrium partitioning approach, while 4,4'-DDE, 4,4'-DDT, and dieldrinare assessed based on consensus-based SQGs (MacDonald et al., 2000)(Table 5-5). Based on the appropriate comparisons, ecological effects are unlikely from exposures of benthic invertebrates to 4,4'-DDE, 4,4'-DDT, dieldrin, and endosulfan I. The remaining COIs (carbazole and methoxychlor) are discussed below.

Carbazole: Table 5-5 compares the 95% UCL of mean carbazole concentrations detected in Lake Erie sediment with the chronic equilibrium partitioning-based benchmark presented in Table 4-2. The maximum detected concentration of carbazole in sediment corrected for 1% TOC (0.57 mg/kg) exceeded the chronic equilibrium partitioning-based benchmark; however, the 95% UCL of the mean concentration does not exceed the benchmark value. The benthic invertebrate benchmark for carbazole is estimated using a highly protective Tier II secondary chronic value (SCV). Tier II SCV values are developed with a limited amount of toxicity data using a set of safety factors, and they are generally more protective than ONWQC and AWQC values. Because the mean detected concentration of carbazole does not exceed the protective benchmark value, adverse effects on benthic invertebrates due to carbazole in Lake Erie sediment are considered to be unlikely.

Methoxychlor: As shown in Table 5-5, the 95% UCL of the mean concentration of methoxychlor slightly exceeds the chronic equilibrium partitioning-based benchmark value. The source of methoxychlor in Lake Erie sediment is uncertain. Methoxychlor was detected in only six of thirty-nine soil samples collected at the Site (Appendix E). Of the six soil samples containing methoxychlor, only the maximum detected concentration is greater than the minimum detected concentration of methoxychlor in Lake Erie sediment. Methoxychlor was not detected in Grand River sediment, and no historical pesticide manufacturing occurred at the Painesville Site. Toxicity to benthic invertebrates due to methoxychlor is possible; however, based on the history of the site, surface soil data, and Grand River sediment data, methoxychlor is not considered to be site-related. Therefore, methoxychlor is not evaluated further.

Inorganic Chemicals

The following inorganic chemicals are assessed in Lake Erie sediment: antimony, total chromium, and cyanide. Based on the appropriate benchmark comparisons (Section 5.1.1.1), ecological effects are unlikely from exposures of benthic invertebrates from antimony and chromium. The potential for sediment toxicity cannot be assessed for cyanide; uncertainty associated with this COI is discussed in Section 5.1.2.

In summary, ten PAHs and Total PAHs pose a probable risk to benthic invertebrates in Lake Erie sediment.

5.1.2 Uncertainty Evaluation

Sources of uncertainty in the risk assessment for benthic invertebrates are related to the selection of chemicals for evaluation and the characterization of exposure and effects.

COI Selection. TICs were removed prior to COI selection. Since the identity and estimated concentrations of TICs are highly uncertain, TIC information was excluded which may result in an under estimation of the chemicals detected at the Site. However, since TICs have a low detection frequency, their elimination does not necessarily result in a reduced COI list.

The COI selection process is based on EDQLs, which are intended to be highly protective. While some EDQLs are based on only limited toxicological information, the conservatism inherent in their derivation should generally prevent detected chemicals from being inappropriately eliminated as COIs. It is not possible to evaluate whether other, unmeasured chemicals have the potential to adversely affect ecological receptors in the study area.

Exposure Assessment. The extent of sediment sampling varies among chemicals and between the two aquatic study areas. Although many analytes were measured in 18 Grand River samples, some chemicals were analyzed in fewer samples, and only four samples from Lake Erie were analyzed for chemical content. However, the COIs evaluated for Lake Erie generally show similar results among the four samples.

An additional source of uncertainty is the assumption that benthic invertebrates may be affected by chemical concentrations in sediment but not surface water. In fact, benthic invertebrates probably are exposed to some extent to elevated concentrations of hexavalent chromium and TDS in surface water. Hexavalent chromium is a COI in sediment but is not evaluated due to a lack of toxicological information; however, total chromium is eliminated as a sediment COI based on comparisons to screening benchmarks. Risks associated with COIs in surface water are evaluated for fish and aquatic invertebrates, and conclusions of this assessment should also be applicable to benthic invertebrates.

Dieldrin in Groundwater – Dieldrin was identified as a COI for groundwater. Dieldrin was not evaluated quantitatively using the BIOSCREEN groundwater model. Rather, dieldrin is evaluated qualitatively here since 1) dieldrin's human health non-drinking water OMZA is 0.0000065 ug/L, far below achievable reporting limits, thus making it impossible to demonstrate compliance using modeling or direct measurement, 2) dieldrin is detected in groundwater at the Site at only four groundwater wells (out of 85 wells) and as "J" estimated values (i.e. below the Practical Quantitation Limit), 3) the Site does not have known past historical uses of dieldrin that would lead to potential sources or source areas on the Site and 4) on-site soils are not a source of dieldrin to groundwater.

A total of 19 dieldrin soil samples slightly exceed the USEPA Region V EDQL of 0.00238 mg/kg, with 12 of the 19 detected as "J" or estimated values. The 7 non-"J" values are scattered in several Parcels (i.e. 1B1, 1C1, 7A1, 7B1, 7C2), confirming that a large persistent source of dieldrin does not exist on the Site.

Effects Assessment. The potential for sediment toxicity cannot be assessed for several sediment COIs due to a lack of toxicological information. These COIs include barium, beryllium, hexavalent chromium, cyanide, selenium, and vanadium. These COIs are evaluated with respect to wildlife receptors, although cyanide is not considered bioaccumulative and is assumed not to be present in wildlife prey.

Incomplete knowledge of site-specific bioavailability is the primary source of uncertainty for COIs that are evaluated for benthic invertebrates. The toxicity of inorganic chemicals is particularly uncertain, as site-specific factors affecting bioavailability are not well understood. For hydrophobic organic chemicals, sediment organic carbon content is used to assess site-specific bioavailability. However, other factors may also influence bioavailability (*e.g.*, differences in the source matrix, which for PAHs may range from petroleum releases to soot particles produced through combustion). The U.S. EPA (1993c) estimates that four to five-fold variation can be expected between observed sediment effects thresholds and those predicted based on equilibrium partitioning for hydrophobic organic chemicals. Others have suggested that the equilibrium partitioning approach may produce benchmarks that are overly protective by several orders of magnitude in some cases, due to the slow rate of desorption from sediment particles for persistent contaminants (Kan *et al.*, 1998).

Risk characterization. For risk characterizations involving comparison to the consensus-based SQGs (e.g., PAHs), the number of sediment samples may be inadequate to predict sediment toxicity within acceptable limits of certainty. MacDonald et al. (2000) evaluated the SQGs for their predictive ability based on a minimum of 20 samples, whereas only four sediment samples were analyzed from Lake Erie and 18 from the Grand River. The limited number of sediment samples could lead to incorrect conclusions about predicted risk, particularly in Lake Erie.

5.1.3 Risk Interpretation

Risks to benthic invertebrates from sediment COIs in the Grand River appear to be indeterminate for most COIs, based on comparisons of chemical concentrations in sediment to screening benchmarks. Invertebrate Community Index (ICI) data, discussed in Section 4.1, indicate an impact to the benthic community is occurring in the vicinity of RM 3.2 to RM 3.5. This risk estimation identified a probable risk to benthic invertebrates from naphthalene in Grand River sediments, suggesting a possible cause for the observed poor ICI scores in the Grand River. Also, as discussed previously in this Section (Exposure Assessment), low ICI scores could also be partly explained by direct exposure of benthic invertebrates to surface water COIs such as hexavalent chromium and TDS.

Benthic invertebrates in Lake Erie adjacent to the Painesville Site are probably adversely affected by PAHs in sediment, based on the comparison of chemical concentrations to literature-based benchmarks. The possibility of effects due to methoxychlor in Lake Erie sediment cannot be eliminated, but such effects are unlikely, and methoxychlor is not considered to be site-related. Therefore, methoxychlor is not evaluated further. This interpretation of risk to benthic invertebrates in Lake Erie sediments cannot be used as the basis for broad conclusions about risk, because it is based on only four sediment samples.

5.2 Fish and Aquatic Invertebrates (Surface Water)

Risks to fish and aquatic invertebrates in the Grand River and Lake Erie shoreline study areas are assessed for all life stages based on the evaluation of COI concentrations in surface water. Risk estimation, uncertainty evaluation, and risk interpretation for fish and aquatic invertebrates in these study areas are presented in the following subsections.

5.2.1 Risk Estimation

Potential risk to fish and aquatic invertebrates in the Grand River is assessed for all life stages based on the evaluation of COI concentrations in surface water. The following surface water COIs are assessed: chromium (total and hexavalent) and TDS. The arithmetic mean and maximum detected concentration of these COIs (Table 3-3) are compared with ONWQC shown in Table 5-3b. The arithmetic mean concentration is compared to a chronic water quality criterion, and the maximum detected concentration is compared to an acute criterion. This type of comparison is appropriate because the mean concentration of each COI is the best approximation of conditions to which aquatic organisms are chronically exposed, whereas the maximum concentration is expected to represent localized or ephemeral conditions which mobile aquatic organisms would encounter only as acute exposures.

The concentration of total chromium in Grand River Surface Water is lower than the appropriate benchmarks and is unlikely to adversely affect aquatic receptors. While the 95% UCL of the mean concentrations of total chromium and hexavalent chromium (unfiltered) are lower than their chronic benchmarks (Table 5-3b), localized exceedances have been noted and these could affect aquatic receptors.

The mean concentration of hexavalent chromium (filtered)(0.013 mg/L) is above the OMZA standard for hexavalent chromium (0.011 mg/L). In 2000 and 2001, there were 57 exceedances of the OMZA standard for Cr (VI). Of these exceedances, the maximum detected concentration was 21 times the OMZA standard, while the majority of exceedances (48) were two times the OMZA standard or less. Periodic exceedences of the OMZM criterion for Cr (VI) have also been observed both within the study area and downstream of the Painesville WPCF. These data indicate that incidences of episodic acute and chronic toxicity to aquatic life are likely affecting biological communities in the Grand River both within the site and downstream. These instances are likely to have both short and long term impacts upon species richness and the abundance of organisms within the river, and may play an important role in the observed partial and non-attainment of the biological water quality criteria in the Grand River.

Hexavalent chromium is toxic to aquatic life because of the strong oxidizing action of chromates and their interaction with organic molecules. Acute (lethal) effects of hexavalent chromium are known to occur in fish at concentrations of 3,400 to 170,000 ug/L depending upon species, life stage and size, and abiotic factors such as water hardness and pH (Eisler 2000). Sublethal effects of hexavalent chromium on aquatic life include behavioral modifications such as avoidance, disrupted feeding, lowered resistance to pathogenic organisms and alterations in population structure. In invertebrates, sublethal effects can occur across a range from 10 ug/L in *Daphnia magna* (reduced survival and fecundity) to 100 ug/L in *Chironomus tentans* larvae (abnormal movement), to 1840 ug/L in the freshwater prawn *Macrobrachium lamarrei* (temporary decrease in hemolymph glucose levels). In fish, sublethal effects in rainbow trout fingerlings can occur at 16 to 21 ug/L (reduced growth), and in bluegill at 50 ug/L (increased locomotor activity) (Eisler, 2000). The hexavalent chromium concentrations measured in the Grand River are generally within these reported ranges of sublethal toxicity to aquatic life.

Based on the observed maximum concentration of total chromium in Grand River surface water, adverse effects due to trivalent chromium are unlikely. Surface water concentrations of hexavalent chromium (total and dissolved) and TDS exceed ONWQC in the Grand River. The detected concentrations are provided in Appendix D.

5.2.2 Uncertainty Evaluation

The risk characterization for fish and aquatic invertebrates is subject to uncertainty with regard to selection of COIs, the exposure assessment for surface water, and the effects assessment for hexavalent chromium and TDS. This section discusses the primary sources of uncertainty and possible biases associated with these uncertainties.

COI Selection. No organic chemicals were analyzed in Grand River surface water. The lack of these data is not likely to affect the conclusions of this assessment. Elevated levels of organic chemicals were not detected in Grand River sediments at levels above screening benchmarks, and site-related surface water impacts are not expected in Lake Erie due to dilution with a large volume of water.

Exposure Assessment. Chemical analyses of surface water provide only a “snap shot” of ambient surface water conditions, which change over time. The use of a limited analytical data set for surface water may overestimate or underestimate risks to fish and aquatic invertebrates. However, this Lake Erie and Grand River Baseline ERA considers a very large database for hexavalent chromium and TDS in Grand River surface water. Thus, spatial and temporal variability of these COIs are unlikely to affect the conclusions of this Lake Erie and Grand River Baseline ERA.

Effects Assessment. Incomplete knowledge of the site-specific bioavailability and toxicity of TDS represents an important source of uncertainty in the effects assessment for fish and aquatic invertebrates. This uncertainty is important, as water quality standards derived from the results of laboratory tests may be overly protective (U.S. EPA, 1985; Bergman and Dorward-King, 1997).

Ohio EPA has established a water quality criterion for TDS, however, surface water toxicity is difficult to predict based on TDS measurements alone. Although osmotic effects are associated with total ion concentrations, toxicity is also influenced by the abundance of specific ions comprising TDS (Ingersoll *et al.*, 1992; Pillard *et al.*, 1996). In the absence of site-specific information regarding toxicity effects of TDS releases from the Painesville Works site, it is impossible to determine toxicity effects for specific ionic constituents upon the biological communities within the Grand River. Therefore, the water quality criterion of 1500 mg/l for TDS continues to be the best indicator for the presence of chronic toxicity related to dissolved ionic constituents with respect to this study.

Calcium, sodium and magnesium concentrations in Grand River surface water at the Site were found to be elevated over background. All three metals are common constituents of Solvay process waste (Hou, 1942). As discussed in detail in Section 2.7.3.3, toxic levels of calcium in environmental media are not reported in the scientific literature. The osmotic effects of sodium could cause a shift in the species composition of aquatic communities to favor more salinity-tolerant species. The maximum detected concentration of sodium in Grand River surface waters was 278 mg/L, or 0.03%. While considerably below the concentration of sodium in sea water (about 1%), sodium at the levels detected could potentially cause some shift in species composition.

5.2.3 Risk Interpretation

The estimated risks to fish and aquatic invertebrates in the Grand River appear to be limited to surface water exposure to elevated hexavalent chromium and infrequently elevated TDS. Toxicological data are lacking for TDS toxicity in surface water. Thus, the risk posed by TDS to surface water is indeterminate.

5.3 Wildlife

The risk characterization for wildlife ROIs includes (1) risk estimation, based on the comparison of estimated exposures (ADDs) to toxicological benchmarks (TRVs), (2) an evaluation of key uncertainties affecting the exposure models for wildlife and the derivation of TRVs, and (3) interpretation of the spatial occurrence of COIs that might elicit adverse effects in ROIs. This approach uses a weight-of-evidence evaluation that integrates quantified risk estimates with relevant information on exposure and effects assumptions and characteristics of COIs. These lines of evidence are used to interpret the likelihood of adverse effects being expressed in real populations of receptors, and to identify key assumptions that could be investigated to reduce the uncertainty of the assessment for wildlife.